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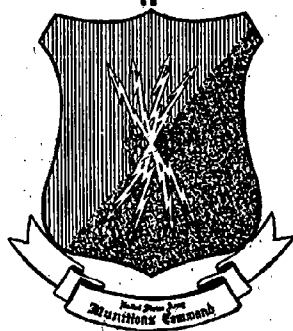
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PICATINNY ARSENAL TECHNICAL REPORT 3072

COBALT-60 GAMMA RADIOLYSIS  
OF LIQUID DINITROGEN TETROXIDE

THOMAS C. CASTORINA

MAY 1963

OMS 5011.11.838.001

DA PROJECT 599-25-001

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PICATINNY ARSENAL  
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COBALT-60 GAMMA RADIOLYSIS  
OF LIQUID DINITROGEN TETROXIDE

BY

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May 1963

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## ABSTRACT

The cobalt-60 gamma radiolysis of liquid dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ )<sub>l</sub> has been investigated as a function of variations in temperature, gas-to-liquid volume ratio, dose rates, and method of ( $\text{N}_2\text{O}_4$ )<sub>l</sub> purification. The radiolytic products are shown to be  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{N}_2\text{O}_5$ . The material balance of the  $\text{O}_2$  released at post-irradiation thermal equilibrium as compared with the calculated  $\text{O}_2$  derived from the production of  $\text{N}_2$  and  $\text{N}_2\text{O}$  from  $\text{N}_2\text{O}_4$  is good to within 10%. ( $\text{N}_2\text{O}_4$ )<sub>l</sub> is relatively radiation-resistant, having a G value of only 0.075, the ratio of  $\text{N}_2$  and  $\text{N}_2\text{O}$  product formation being 2:1. The independence of product yields in relation to changes in dose rate indicates that radical-molecule processes are involved in product formation. An apparent induction period, observed at 0.4 Mrad per hour, is also shown to be independent of dose rate. The addition of argon to ( $\text{N}_2\text{O}_4$ )<sub>l</sub> has no effect on the radiolytic yields. The addition of  $\text{O}_2$ , over the partial pressure range of 200-350 mm, results in a G value for  $\text{N}_2\text{O}_5$  formation that is in excellent agreement with that for  $\text{N}_2\text{O}_5$  formation from pure ( $\text{N}_2\text{O}_4$ )<sub>l</sub>. Although the addition of  $\text{O}_2$  has no effect on the  $\text{N}_2\text{O}$  formation, the induction period for  $\text{N}_2$  is eliminated and the amount of  $\text{N}_2$  is decreased by 80%.

## INTRODUCTION

The nitro group is considered to be one of the most important phosphoric groups in Ordnance chemistry. When substituted in an organic molecule in sufficient numbers, it supplies the necessary oxygen balance for the complete conversion of the carbons and hydrogen to carbon dioxide and water. The problem has been to effect the maximum number of substitutions possible without degrading the parent molecule in the process. Conventional methods of synthesis are rapidly exhausting all avenues of approach to a solution to this problem. New methods must be investigated, one such method being preparative radiation chemistry.

High-energy radiation is known to produce the already familiar entities, carbonium and nitronium ions, free radicals and excited molecules in environments devoid of high pressures and temperatures, stringent oxidizers and catalysts. This might make possible modifications and improvements in existing methods of synthesis that depend on their reactions. Even more important, however, is the possibility that high-energy radiation, e.g., cobalt-60 gammas, may afford a unique method of forming different active intermediates, capable of undergoing new types of reactions not so much in quantity but in kind as an indication that the resultant new compounds can and do exist. Since  $\text{NO}_2$  normally exists in equilibrium with dinitrogen tetroxide, it is more than likely that liquid dinitrogen tetroxide  $(\text{N}_2\text{O}_4)_l$  when subjected to ionizing radiation could become a good source not only of  $\text{NO}_2$  radicals but of ionic and excited  $\text{NO}_2$  molecules as well. The concurrent existence of such a variety of active intermediates in situ may open a whole new field of nitrolysis.

Before a study can be made of a two-component system, as would be the case in preparative radiation chemistry, the radiolysis of each component should be studied separately. For a two-component system consisting of benzene and  $(\text{N}_2\text{O}_4)_l$ , only one of the components needs investigation. The radiation chemistry of benzene is fairly well established and benzene has been found to be relatively resistant to gamma fields (Ref 1). However, the radiolysis of nitrogen dioxide, in its dimeric form, as a liquid, has not been reported in the literature. The radiolysis of nitrogen dioxide gas in a nuclear reactor has been studied by Harteck and Dondes (Ref 2) and, more recently, Dimitriev and Saradzhev (Ref 3) have reported on the gamma radiolysis of gaseous  $\text{N}_2\text{O}_4$  at varying intensities and pressures. For the present study, an investigation of the cobalt-60 gamma radiolysis of  $(\text{N}_2\text{O}_4)_l$  was considered more appropriate to subsequent investigations involving its radiation-induced reac-

tions with aromatics and possibly aliphatics. Diamagnetic  $(\text{N}_2\text{O}_4)_1$  is transparent over a wide range of wavelengths. The series of light straw to brown-red colors imparted to the liquid is due to the presence of the paramagnetic  $\text{NO}_2$  monomer. In the saturated vapor phase,  $\text{N}_2\text{O}_4$  dissociates 8.6% at  $-11.2^\circ\text{C}$  (MP) and 15.9% at  $21.2^\circ\text{C}$  (BP). In the liquid phase, the dissociation of  $\text{N}_2\text{O}_4$  occurs to the extent of 0.018% at  $-11.2^\circ\text{C}$  and 0.12% at  $21.2^\circ\text{C}$  (Ref 4).

## DISCUSSION AND RESULTS

Using tank gas,  $(\text{N}_2\text{O}_4)_1$  of high purity was prepared by sparging with purified oxygen to convert lower oxides to  $\text{N}_2\text{O}_4$ . Trace quantities of moisture were removed with phosphorus pentoxide. The liquid was degassed a minimum of three times at  $-78^\circ\text{C}$ . The center fractions, which were protected from stopcock grease contamination by glass bead traps, were distilled into 5-cc pyrex break seals for irradiation studies. Samples were irradiated at  $20^\circ\text{C}$  in a cobalt-60 gamma field of approximately  $4 \times 10^5$  r/hr.

The irradiated samples were degassed at liquid nitrogen temperature ( $-196^\circ\text{C}$ ) and the gases isolated at this temperature were analyzed mass spectrometrically and found to consist of only nitrogen and oxygen. The relative amounts of each constituent were calculated from their respective mass peak heights. As a check, the amount of oxygen was also determined by its reaction with hydrogen at the catalyzing surface of a heated (barely perceptible glow point) platinum filament. The results listed in Table 1 show the two methods to be in good agreement.

In the process of making these initial determinations, 5 to 6 sample batches of  $(\text{N}_2\text{O}_4)_1$  had been irradiated together for the same period of time. Upon removal from the source they were placed under refrigeration at  $2-5^\circ\text{C}$  and taken as needed for analysis over a period of 2 days. When this was done, it was observed that the percentage of oxygen gradually increased with each successive sample analysis. This was indicative of the existence of a thermally unstable product of radiolysis which decomposed with the evolution of oxygen. In establishing the post-irradiation gaseous product(s) of thermal decomposition the following assumptions were made: (a) that oxygen was the only gas released after radiation, and (b) that nitrogen was a direct product of radiolysis, independent of the amount of oxygen present at any one time after radiolysis. To demonstrate the validity of these assumptions, an extensive series of  $(\text{N}_2\text{O}_4)_1$  samples were irradiated with various doses. The irradiated samples were analyzed at irregular intervals during the post-irradiation

TABLE 1  
Comparative Analysis of Gaseous Products  
Isolated at -196° C

Platinum Filament Analysis <sup>a</sup>		Mass Spectrometric Analysis <sup>b</sup>	
Percent Oxygen	Percent Nitrogen	Percent Oxygen	Percent Nitrogen
3.6	96.4	3.5	96.5
3.4	96.6	3.6	96.4
5.7	94.3	6.5	93.5
5.4	94.6	6.4	93.6
3.6	96.4	5.7	94.3
25.8	74.2	26.0	74.0
43.5	56.5	44.8	55.2
50.7	49.3	50.9	49.1
65.3	34.7	66.9	33.1
65.5	34.5	65.7	34.3

<sup>a</sup>Percent composition of N<sub>2</sub> by difference

<sup>b</sup>Based on relative ratios of respective mass peaks. (N<sub>2</sub> and O<sub>2</sub> were the only gases present.)

period. The random distribution of oxygen was subtracted from the gas mixture isolated at  $-196^{\circ}\text{C}$  and all values were reported in terms of nitrogen formed. These results are listed in Table 2. A plot of the cc of  $\text{N}_2$  at STP per gram of  $(\text{N}_2\text{O}_4)_1$  versus the dose in megarads is given in Figure 1. The curve obtained shows an apparent induction period which may represent that time interval where intermediate species are increasing in sufficient concentrations for final conversion to stable radiolytic products. It is also possible that this induction period is due to the presence of trace quantities of impurities which are scavenging the intermediates, momentarily preventing the formation of products of radiolysis. Following this induction period there is a straight line portion of the curve from 15 to 50 megarads corresponding to a constant  $G(\text{N}_2)$  of 0.052. This constant  $G$  value demonstrates the independence of  $\text{N}_2$  product formation from variations in the amount of  $\text{O}_2$ , and thereby demonstrates further that  $\text{N}_2$  is a direct product of radiolysis. It was therefore concluded that the post-irradiation thermal decomposition of one of the products of radiolysis involves the evolution of  $\text{O}_2$  only.

At the outset of this work, extreme difficulty was experienced in preparing ampoules of liquid  $\text{N}_2\text{O}_4$  devoid of free space. This was due to the relatively high thermal coefficient of expansion of  $(\text{N}_2\text{O}_4)_1$ ,  $2.4 \times 10^{-3}\text{cc}$  increase per unit cc per degree centigrade rise (greater than that of ethyl ether). It therefore became necessary to determine the effect of the presence of various volumes of gas in equilibrium with the liquid on the  $G$  values and mechanism of product formation.  $G$  value is defined as the number of molecules, either decomposed or formed, per 100 electron volts of energy absorbed. Table 3 shows that the  $G(\text{N}_2)$  is independent of variations in the ratio of gas-to-liquid volumes over a factor range of approximately 600. The ratio of 0.004 represents a liquid sample with a volume of 0.02 cc of gas confined in the one mm capillary end of the break-seal. It was therefore concluded that in calculating  $G$  values, variations in the volume of gas in equilibrium with the liquid could be ignored, where the weight of the gas is always negligible in comparison with that of the liquid. The calculation of the  $G$  value, based on the ferrous sulfate dosimeter was, as a result, corrected only for the electron density difference of  $(\text{N}_2\text{O}_4)_1$ . In addition, the data listed in Table 3 signifies that nitrogen formation is derived from a liquid intermediate since the  $G(\text{N}_2)$  remains constant as the volume of gas increases.

To determine how critical the control of temperature is during long periods of irradiation, a series of samples of  $(\text{N}_2\text{O}_4)_1$  was irradiated at

TABLE 2  
Independence of  $N_2$  Formation With Variations in the Concentration of  
Oxygen

Hours Irradiation	Dose M rads	Grams ( $N_2O_4$ ) <sub>1</sub>	cc ( $N_2$ ) STP per g ( $N_2O_4$ ) <sub>1</sub>	cc ( $O_2$ ) STP per g ( $N_2O_4$ ) <sub>1</sub>
12	4.92	6.326	0.0012	0.0001
12	4.92	5.991	0.0005	0.0001
24	9.84	6.500	0.0034	0.0001
24	9.84	6.225	0.0035	0.0091
36	14.76	6.324	0.0078	0.0005
36	14.76	6.176	0.0074	0.0082
48	19.68	5.768	0.0123	0.0005
48	19.68	6.187	0.0122	0.0459
72	29.52	6.190	0.0276	0.0770
72	29.52	6.178	0.0279	0.0025
96	39.36	5.934	0.0365	0.0987
96	39.36	5.855	0.0365	0.0152
96	42.14	2.423	0.0418	0.0434
96	42.14	6.161	0.0421	0.0914
96	42.14	5.577	0.0410	0.0121
120	49.20	6.305	0.0490	0.0139
120	49.20	5.420	0.0546	0.1296
120	49.20	6.095	0.0485	0.0132
120	52.68	5.082	0.0566	0.0140
120	52.68	5.184	0.0562	0.1246



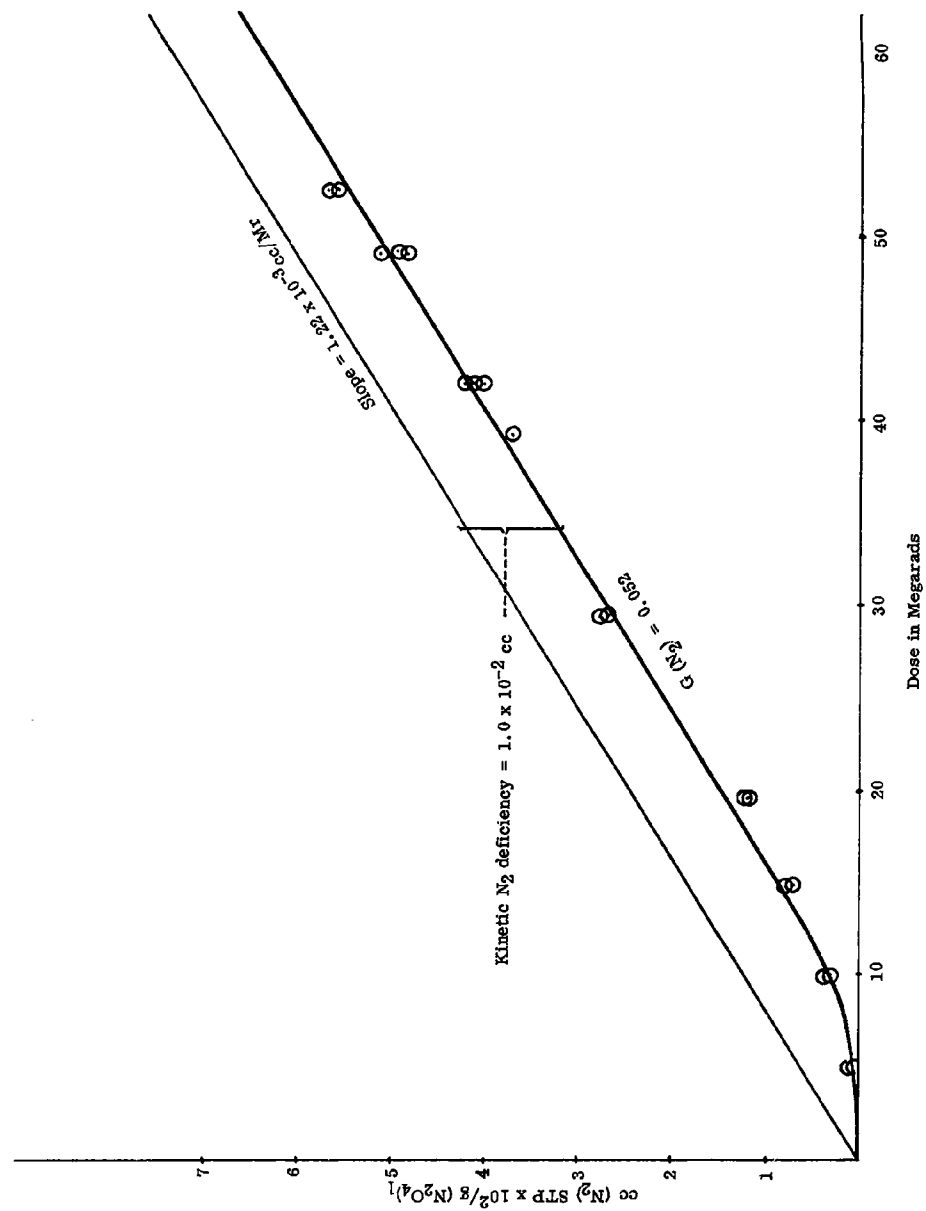


Figure 1. Cobalt-60 Gamma Radiolysis of Liquid N<sub>2</sub>O<sub>4</sub> at 20°C. Dependence of Nitrogen Formation on Dose

TABLE 3

Independence of  $G(N_2)$  in Relation to Variations in

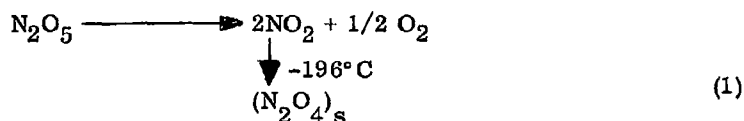
Volume $(N_2O_4)_g$ : Volume $(N_2O_4)_l$ Ratio		
Dose in Rads ( $\times 10^{-7}$ )	$G(N_2)$	Vol $(N_2O_4)_g$ : Vol $(N_2O_4)_l$
4.92	0.048	0.031
4.92	0.047	0.050
4.92	0.053	0.100
5.27	0.051	0.307
5.27	0.051	0.348
4.21	0.048	0.877
4.21	0.047	2.318
4.21	0.049	0.952
4.21	0.047	1.637
4.21	0.046	0.114
4.21	0.048	0.035
2.18	0.045	0.004

Average  $G(N_2) = 0.048 \pm 0.002$

at different temperatures. The  $G(N_2)$  was observed to remain constant over a temperature range of  $0^\circ$  to  $30^\circ\text{C}$ . The results of these experiments are summarized in Table 4. However, in spite of this apparent insensitivity of  $G(N_2)$  to temperature fluctuations in this range, irradiations throughout this investigation were conducted at  $20^\circ\text{C} \pm 1^\circ$ .

#### Kinetics of $N_2O_5$ Decomposition in $(N_2O_4)_l$

In consideration of the fact that some oxides of nitrogen are thermally unstable at room temperature, all oxides lower than nitrogen dioxide were ruled out. For example, nitrous oxide ( $N_2O$ ) is especially stable at these temperatures and nitric oxide ( $NO$ ) as well as  $N_2O_3$  combine readily with the available oxygen of irradiated samples to form  $NO_2$  and/or  $N_2O_4$ . On the basis of the results shown in Table 2, this oxide decomposes to  $O_2$  plus some product condensable at  $-196^\circ\text{C}$ , i.e., the temperature at which the degassing of samples is performed. This would be analogous to:



The original studies on the rate of decomposition of nitrogen pentoxide are classics in the field of kinetics and the reaction is reported to be first order over a wide range of temperatures and pressures. As a standard for comparison in the process of identifying the unknown kinetically, Eyring and Daniels' published data on the decomposition of  $N_2O_5$  in  $(N_2O_4)_l$  was used (Ref 5). The rates of decomposition based on the rates of oxygen evolution after radiolysis were determined at  $20^\circ$ ,  $22^\circ$ , and  $25^\circ\text{C}$ , on sets of five samples. Each set was irradiated together for a total of 96 hours, equivalent to  $4 \times 10^7$  rads. Included with this set was one sample which was quenched in a dry-ice bath directly upon removal from the source. Analysis of this sample gave the concentration of  $N_2O_5$  at zero time after irradiation. A second sample was included that gave the total concentration of the  $N_2O_5$  for the set, upon thermal equilibration. For each particular run, the five samples were placed in a constant temperature bath directly after radiolysis and removed from time to time for oxygen analysis. This data, in terms of cc ( $O_2$ ) STP per gram of  $(N_2O_4)_l$  as a function of time, together with the corresponding fractions remaining (assumed to be  $N_2O_5$ ), is shown in Table 5. The fraction of  $N_2O_5$  remaining, plotted on the logarithmic scale versus the time in hours, is shown in Figure 2. The straight lines obtained on this semilog plot for each of the temperatures studied indicate first order kinetics.

TABLE 4  
Independence of  $G(N_2)$  in Relation to Radiolysis of  
 $(N_2O_4)_1$  at Various Temperatures

Dose in Megarads	Temp °C $\pm 1^\circ$	$G(N_2)$	Average $G(N_2)$	Average Deviation
39.36	0	0.048	0.047	$\pm 0.001$
39.36	0	0.048		
39.36	0	0.047		
39.36	0	0.047		
39.36	0	0.046		
39.36	15	0.045	0.048	$\pm 0.003$
39.36	15	0.045		
49.20	15	0.048		
49.20	15	0.053		
42.14	20	0.047	0.048	$\pm 0.001$
42.14	20	0.049		
42.14	20	0.047		
42.14	20	0.048		
49.20	20	0.047		
52.68	20	0.051		
26.40	30	0.049	0.048	$\pm 0.001$
26.40	30	0.047		

TABLE 5  
Post Irradiation Rate of  $N_2O_5$  Decomposition as a Function of Temperature <sup>a</sup>

$^{\circ}C \pm 0.05$	mm Gas ( $N_2+O_2$ )	Percent $O_2$	Grams ( $N_2O_4$ )	$cc(O_2)$ STP $g(N_2O_4)$	$^{\circ}K$	Fraction $N_2O_5$ Remaining <sup>b</sup>	Seconds ( $\times 10^{-4}$ )	Spec Rate Const. ( $\times 10^4 \text{ sec}^{-1}$ )
20	118.2	31.8	7.052	1.96	294.5	0.820	0 <sup>c</sup>	0.103
20	140.5	47.5	7.025	3.48	296.6	0.681	1.8	0.106
20	173.8	53.7	7.010	4.87	295.8	0.584	3.6	0.104
20	189.5	62.3	6.490	6.68	295.4	0.387	7.2	0.103
20	179.2	65.7	5.400	7.98	296.0	0.268	10.8	0.100
20	246.0	68.5	6.887	9.00	295.5	0.176	16.2	0.100
20	263.0	72.5	6.420	10.90	295.4	0	$\rightarrow \infty$ d	0.103
22	84.8	19.4	5.790	1.035	297.5	0.902	0 <sup>c</sup>	0.14
22	102.0	36.2	5.595	2.40	297.5	0.773	1.08	0.15
22	145.4	53.2	5.895	4.78	297.2	0.547	3.24	0.13
22	180.0	60.4	6.150	6.46	296.7	0.389	6.48	0.13
22	202.2	65.4	6.123	7.84	298.2	0.257	9.72	0.14
22	235.6	69.6	6.270	9.58	296.4	0.096	16.2	0.14
22	244.0	71.6	6.038	10.56	297.0	0	$\rightarrow \infty$ d	0.14
25	78.0	20.1	5.300	1.08	296.5	0.905	0 <sup>c</sup>	0.24
25	128.2	52.3	5.230	4.67	297.5	0.588	1.8	0.25
25	157.6	62.0	5.310	6.72	297.0	0.408	3.24	0.23
25	200.5	68.0	5.500	9.06	296.2	0.202	6.48	0.24
25	218.0	70.6	5.470	10.25	297.0	0.097	9.72	0.23
25	235.7	71.9	5.580	11.10	296.5	0.022	16.2	0.23
25	241.2	72.2	5.510	11.35	296.0	0	$\rightarrow \infty$ d	0.23
25	91.0	14.0	7.200	0.646	296.0	0.935	0 <sup>c</sup>	0.25
25	160.7	50.8	7.314	4.09	295.2	0.589	1.8	0.24
25	192.0	61.0	6.817	5.99	294.6	0.398	3.6	0.24
25	227.0	65.5	7.300	7.42	297.0	0.254	5.4	0.23
25	250.5	69.5	7.483	8.52	296.2	0.144	8.28	0.23
25	267.0	72.0	7.050	9.95	297.2	0	$\rightarrow \infty$ d	0.23

<sup>a</sup> All samples irradiated simultaneously for 96 hours ( $4.1 \times 10^5 \text{ r/hr}$ ).

<sup>b</sup> In terms of  $cc(O_2)/g(N_2O_4)$  evolved with time, relative to the amount evolved at  $t \rightarrow \infty$ .

<sup>c</sup> Quenched in dry-ice bath directly after removal from source.

<sup>d</sup> Thermally equilibrated 7 days at  $25^{\circ}C$ .

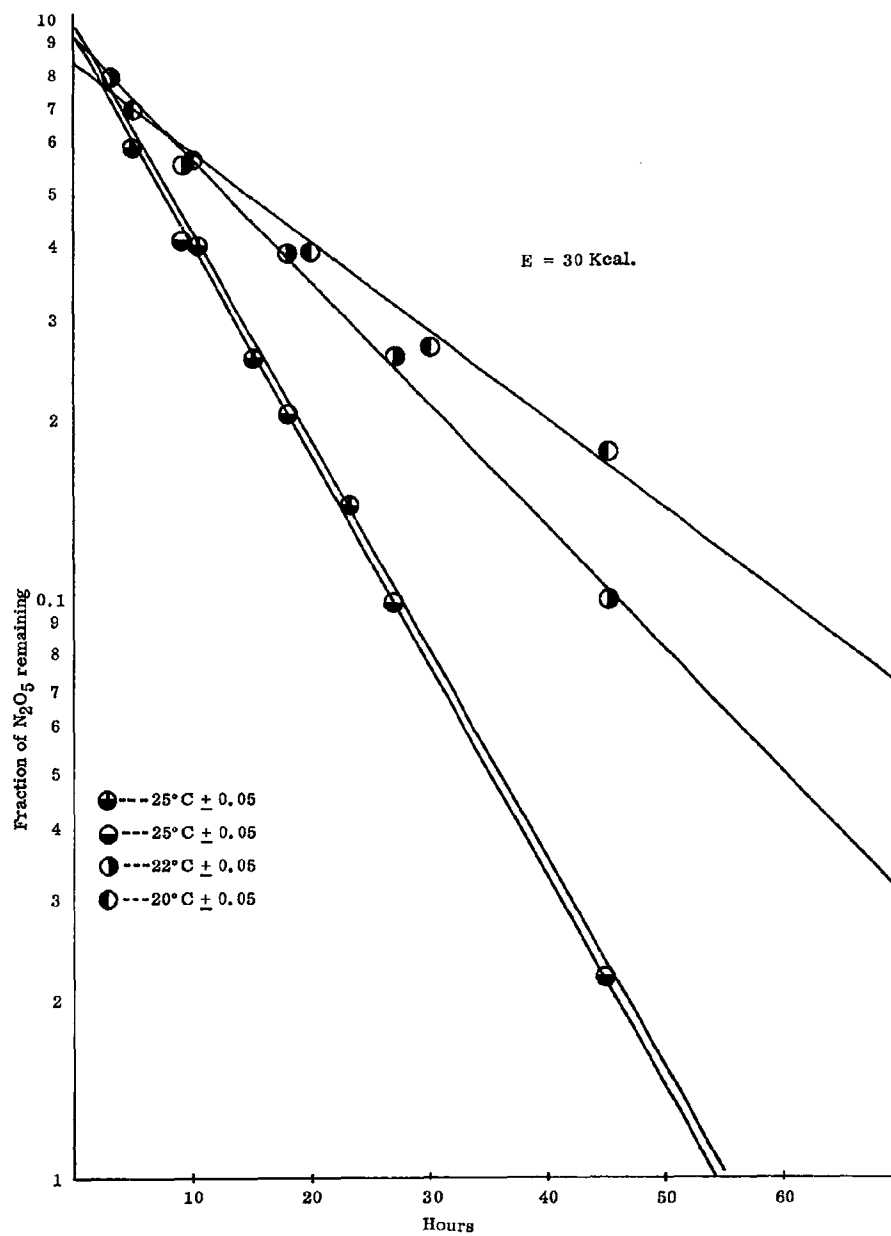
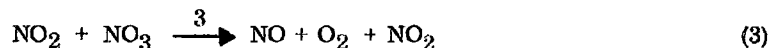


Figure 2. Post Irradiation Rate of  $\text{N}_2\text{O}_5$  Decomposition as a Function of Temperature

As a check, the kinetics of decomposition of synthetic solutions of  $\text{N}_2\text{O}_5$  in  $(\text{N}_2\text{O}_4)_1$  were determined and compared to those obtained by Eyring and Daniels. Synthetic solutions were prepared by ozonizing pure  $(\text{N}_2\text{O}_4)_1$  just sufficiently to give millimolar concentrations of  $\text{N}_2\text{O}_5$ , comparable to those of the irradiated samples, here again assumed to be  $\text{N}_2\text{O}_5$ . The solutions were then degassed twice at  $-78^\circ\text{C}$  and transferred to radially arranged ampoules connected to a common center. The ampoules were finally flame-sealed, placed in a constant temperature bath, and removed from time to time for oxygen analysis. The reproducibility of the sample preparations is shown by the data listed in Table 6. The rates of  $\text{N}_2\text{O}_5$  decomposition in such concentrations were determined at  $20^\circ$  and  $25^\circ\text{C}$  in the same manner as for the irradiated  $(\text{N}_2\text{O}_4)_1$  samples. Table 7 lists the rates of  $\text{O}_2$  evolution and related  $\text{N}_2\text{O}_5$  decompositions. A plot of the log of the fraction of  $\text{N}_2\text{O}_5$  remaining versus time (Fig 3) also shows first order kinetics.

The specific rate constants were calculated directly from the data rather than from the curves, using the first order expression. This was done for both the irradiated and synthetic solutions and results were found to be constant to within 5%.

Table 8 gives a comparison of these specific rate constants. At  $20^\circ\text{C}$ , the average rate constant of the synthetic solutions is in very good agreement with that of the irradiated samples. The higher value reported by Eyring and Daniels is attributed to a concentration effect. At the time their work was reported, the decomposition of  $\text{N}_2\text{O}_5$  was thought of as a unimolecular first order reaction. Since then, the reaction has been shown by Ogg (Ref 6) to be a complex one, as follows:



Empirically, Eyring and Daniels did find an apparent concentration effect in carbon tetrachloride solutions of  $\text{N}_2\text{O}_5$  in that more dilute concentrations decompose at slower rates. It will be noticed that the activation energies in all three cases compare favorably. These kinetic data

TABLE 6

Reproducibility of Sample Preparation of  
Synthetic Solutions of  $\text{N}_2\text{O}_5$  in  $(\text{N}_2\text{O}_4)_1$

No. Moles $\text{N}_2\text{O}_5$ ( $\times 10^4$ ) per sample Vol., cc	Milli Molar Concentration of $\text{N}_2\text{O}_5$ in $(\text{N}_2\text{O}_4)_1$	Average Per- cent Deviation
0.434/4.13	10.5	2.3
0.368/3.63	10.1	
0.370/3.78	9.8	
0.754/3.55	21.2	2.8
0.638/3.17	20.1	
0.250/4.30	5.8	1.7
0.238/4.21	5.7	



TABLE 7  
Rate of Decomposition of Synthetic Solutions of  $\text{N}_2\text{O}_5$  in  $(\text{N}_2\text{O}_4)$  with Temperature

$^{\circ}\text{C} \pm 0.05^{\circ}$	mm Gas ( $\text{N}_2 + \text{O}_2$ )	mM $\text{N}_2\text{O}_5$	Grams ( $\text{N}_2\text{O}_4$ ) <sup>1</sup>	cc ( $\text{O}_2$ ) STP $\frac{\text{g}(\text{N}_2\text{O}_4)^1}{(\times 10^2)}$	$^{\circ}\text{K}$	Fraction $\text{N}_2\text{O}_5$ Remaining <sup>b</sup>	Seconds ( $\times 10^{-4}$ )	Spec. Rate Const. ( $\times 10^4 \text{ sec}^{-1}$ )
20	0	0 <sup>a</sup>	5.280	0	297.0	1.0	$\rightarrow \infty$ <sup>c</sup>	
20	116 <sup>d</sup>	4.0	5.077	0.32	296.6	0.814	1.8	0.12
20	182	4.0	5.166	0.76	297.5	0.558	4.32	0.14
20	212	4.0	5.128	1.05	296.5	0.386	8.64	0.11
20	242	4.0	5.380	1.29	297.4	0.250	12.96	0.11
20	273	4.0	5.16	1.72	296.0	0	$\rightarrow \infty$ <sup>c</sup>	
20	0	0 <sup>a</sup>	6.180	0	297.0	1.0	$\rightarrow \infty$ <sup>c</sup>	
20	12.5 <sup>e</sup>	7.4	6.110	0.748	295.0	0.867	1.08	0.14
20	36.0	7.4	6.202	2.13	296.0	0.622	3.60	0.11
20	57.0	7.4	6.541	3.19	296.0	0.434	7.20	0.12
20	76.0	7.4	6.510	4.27	297.0	0.243	12.96	0.11
20	105.0	7.4	6.784	5.64	297.0	0	$\rightarrow \infty$ <sup>c</sup>	
25	0	0 <sup>a</sup>	6.020	0	297.0	1.0	$\rightarrow \infty$ <sup>c</sup>	
25	17.0 <sup>e</sup>	3.0	5.550	1.12	297.0	0.524	1.8	0.36
25	26.0	3.0	5.530	1.73	295.0	0.264	3.6	0.37
25	31.0	3.0	5.710	1.98	297.0	0.157	5.4	0.34
25	36.5	3.0	6.230	2.15	295.3	0.082	7.2	0.35
25	37.0	3.0	5.980	2.24	297.0	0.046	9.0	0.34
25	38.0	3.0	5.906	2.35	297.2	0	$\rightarrow \infty$ <sup>c</sup>	

<sup>a</sup> Control - pure  $(\text{N}_2\text{O}_4)$ .

<sup>b</sup> In terms of cc ( $\text{O}_2$ )/g  $(\text{N}_2\text{O}_4)$  evolved with time, relative to the amount evolved at  $t \rightarrow \infty$ .

<sup>c</sup> Thermally equilibrated for 7 days at  $25^{\circ}\text{C}$ .

<sup>d</sup> Pressure readings taken at capillary end of McLeod gauge.

<sup>e</sup> Pressure adjusted to 2.39 cc volume.

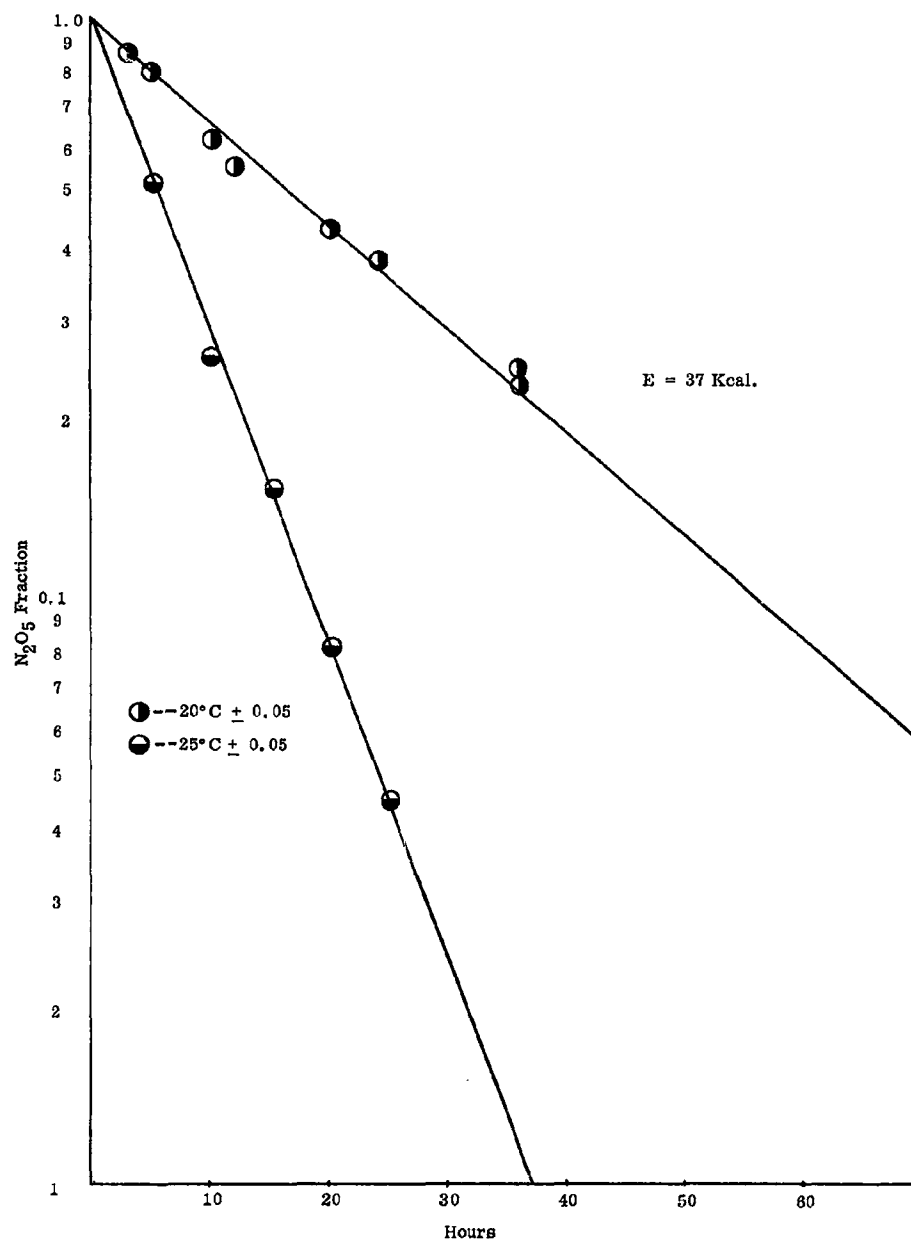


Figure 3. Rate of Decomposition of  $\overline{4.8 \text{ m M}}$  Solution of  $\text{N}_2\text{O}_5$  in  $(\text{N}_2\text{O}_4)_1$  as a Function of Temperature

TABLE 8  
Comparative Specific Rate Constants of  $N_2O_5$  Decomposition in  $(N_2O_4)_1$   
for Synthetic and Radiolytic Solutions<sup>a</sup>

Synthetic Solution of $N_2O_5$ in $(N_2O_4)_1$ Specific Rate Constant <sup>b</sup> ( $\times 10^4 \text{ sec}^{-1}$ )		Radiolytic Solution of $N_2O_5$ in $(N_2O_4)_1$ Specific Rate Constant ( $\times 10^4 \text{ sec}^{-1}$ )		
$20^\circ C \pm 0.05^\circ$	$25^\circ C \pm 0.05^\circ$	$20^\circ C \pm 0.05^\circ$	$22^\circ C \pm 0.05^\circ$	$25^\circ C \pm 0.05^\circ$
0.14	0.36	0.10	0.14	0.24
0.11	0.37	0.11	0.15	0.25
0.12	0.34	0.10	0.13	0.23
0.11	0.35	0.10	0.13	0.23
0.12	0.34	0.10	0.14	0.23
0.14		0.11 <sup>c</sup>		0.25
0.11				0.24
0.11				0.24
				0.23
Avg = 0.12	Avg = 0.35	Avg = 0.10	Avg = 0.14	Avg = 0.24
E = 37 kcal		E = 30 kcal		

<sup>a</sup>Calculations based on remaining fraction of  $N_2O_5$  derived from cc  $(O_2)/$  gm  $(N_2O_4)_1$  evolved with time relative to amount evolved at  $t \rightarrow \infty$ .

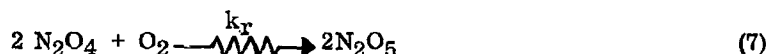
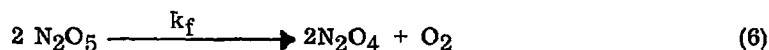
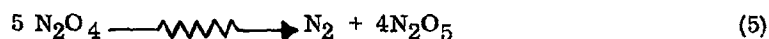
<sup>b</sup>Eyring and Daniels report  $0.344 \times 10^{-4} \text{ sec}^{-1}$  at  $20^\circ C$  and  $E = 26 \text{ kcal}$  for 0.2M solutions of  $N_2O_5/(N_2O_4)_1$ .

<sup>c</sup>Nitrogen sparged.

clearly establish the identity of the thermally unstable product of liquid  $\text{N}_2\text{O}_4$  radiolysis to be  $\text{N}_2\text{O}_5$ . The slight increase in  $k$  for the synthetic solutions as compared to the irradiated solutions might result from the presence of some unreacted ozone remaining in the synthetic solutions.

Notwithstanding the substantial kinetic evidence for the presence of  $\text{N}_2\text{O}_5$  attempts were made to identify  $\text{N}_2\text{O}_5$  directly in situ. However, by virtue of the m Molar concentrations of  $\text{N}_2\text{O}_5$  involved in this study, together with its chemical instability, direct analysis proved most difficult. The methods of analysis employed included Electron Paramagnetic Resonance (EPR) and Vapor Phase Chromatography (VPC). Both irradiated samples and synthetic solutions of  $\text{N}_2\text{O}_5$  in  $(\text{N}_2\text{O}_4)_1$ , after twelve successive fractionations, failed to show differences in their respective VPC spectra from a reference standard consisting of  $(\text{N}_2\text{O}_4)_1$  alone. The EPR spectra obtained for these samples at  $-196^\circ\text{C}$  are extremely complex and can be interpreted only by means of detailed calculations.

It had been noted earlier in this work that the percent of oxygen at near zero time after 48 hours of irradiation was only 3.5%. This suggests the possibility that the rate of decomposition of  $\text{N}_2\text{O}_5$  is initially repressed in a gamma field where the velocity of the reverse reaction is faster than that of the forward reaction



where  $k_r > k_f$ .

This rate of  $\text{N}_2\text{O}_5$  decomposition during irradiation at  $20^\circ \pm 1^\circ\text{C}$  was determined by quenching the thermal reaction in a dry ice bath directly after removal from the source (designated: zero-time-after-radiolysis) at various time intervals and analyzing for the fraction of  $\text{N}_2\text{O}_5$  remaining. The data shown in Table 9 gives the rate of oxygen evolution with the relative fractions of  $\text{N}_2\text{O}_5$  remaining as a function of irradiation time. A graphical representation of this rate in comparison to the rate at the same temperature after radiation (shown in Figure 4) forcefully demonstrates the stabilizing effect of gammas on  $\text{N}_2\text{O}_5$  in  $(\text{N}_2\text{O}_4)_1$ .

TABLE 9

Rate of  $\text{N}_2\text{O}_5$  Decomposition During Irradiation<sup>a</sup> at  $20^\circ\text{C} \pm 1.0^\circ$ 

Grams ( $\text{N}_2\text{O}_4$ ) <sub>1</sub>	mm Gas ( $\text{N}_2 + \text{O}_2$ )	Percent $\text{O}_2$	$^\circ\text{K}$	$\frac{\text{cc}(\text{O}_2) \text{ STP}}{\text{g} (\text{N}_2\text{O}_4)_1 (\times 10^2)}$	Seconds ( $\times 10^{-4}$ )	Fraction <sup>b</sup> $\text{N}_2\text{O}_5$ rem.
5.830	21.4	7.0	296.5	0.10	17.28	0.978
7.070	122.0	72.0	296.1	4.50	$\rightarrow \infty^c$	0
6.178	50.5	8.5	296.3	0.27	25.92	0.964
6.190	50.2	9.6	297.8			
7.154	202.0	71.6	296.0	750	$\rightarrow \infty^c$	0
6.161	81.8	13.2	296.5	0.81	34.56	0.926
4.525	59.0	20.5	294.5			
5.510	241.2	72.2	296.0	11.35	$\rightarrow \infty^c$	0
5.082	99.8	22.0	296.2	1.48	43.20	0.901
5.184	99.5	19.5	296.4			
6.500	348.3	71.9	296.7	14.06	$\rightarrow \infty^c$	0

<sup>a</sup> At a dose rate of 0.41 Mrad/hr.<sup>b</sup> In terms of  $\text{cc}(\text{O}_2)/\text{g}(\text{N}_2\text{O}_4)_1$  evolved with time relative to the amount evolved at  $t \rightarrow \infty$ <sup>c</sup> Thermally equilibrated for 7 days at  $25^\circ\text{C}$ .

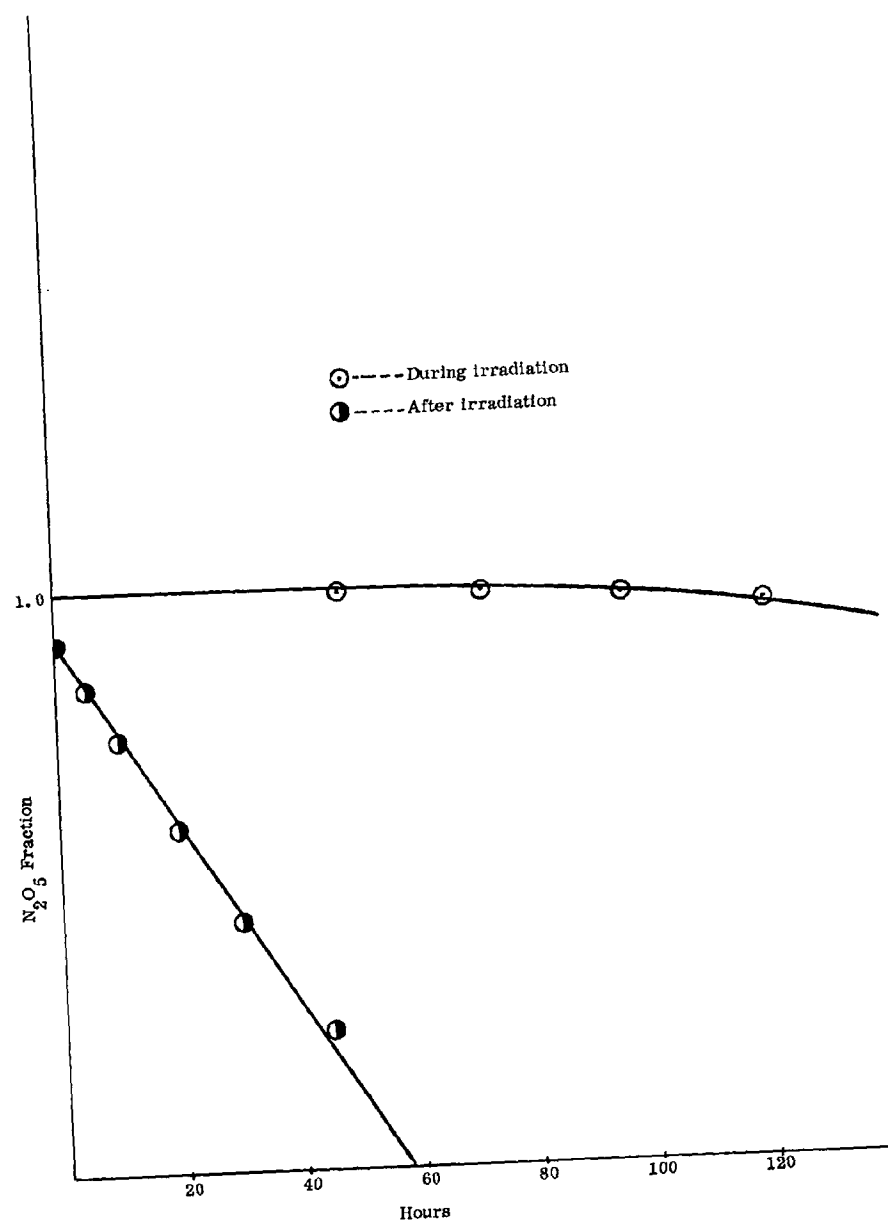
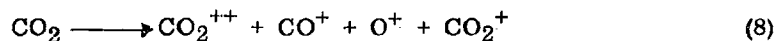


Figure 4. Relative Rates of  $\text{N}_2\text{O}_5$  Decomposition During and After Irradiation at  $20^\circ\text{C}$

## Identification of N<sub>2</sub>O

When the kinetics of decomposition of the thermally unstable product of radiolysis had been established, it became possible to investigate the existence of additional radiolytic products. A series of samples was irradiated 96 hours and thermally equilibrated for 7 days at 25° C. Control samples (i. e., unirradiated (N<sub>2</sub>O<sub>4</sub>)<sub>1</sub>) were included in this determination as in all determinations made in this study. As soon as the equilibrated samples had been degassed at -196° C and analyzed for O<sub>2</sub> and N<sub>2</sub> contents in the usual manner, a second degassing was performed at -130° C. At this temperature, (N<sub>2</sub>O<sub>4</sub>)<sub>g</sub> has no vapor pressure; hence, any gas collected would be either N<sub>2</sub>O or possibly CO<sub>2</sub> as a contaminant. The gas collected was analyzed mass spectrometrically and the spectrum of the mass peaks was compared to those of the CO<sub>2</sub> and N<sub>2</sub>O standards (Table 10). The peak height intensity ratios of the mass to charge ratios of the various combinations of the fragmentation fractions were used to identify the unknown gas. The values given in Table 11 compare well with those of the N<sub>2</sub>O standard. In addition, it should be emphasized that the spectrum of the unknown had a strong 30 peak but contained no trace of a 22 peak. According to the spectrum of the CO<sub>2</sub> standard, the following fragmentation takes place:



While the spectrum of the CO<sub>2</sub> standard contains a 22 peak but no 30 peak, that of the N<sub>2</sub>O standard has a strong 30 peak but no 22 peak. It was therefore concluded that, on the basis of the mass spectrometric data, the gas fractionated at -130° C was N<sub>2</sub>O. This conclusion was further substantiated by the results obtained with the Beckman vapor phase chromatography unit using silica gel heated at 40° C as the absorbing medium. The retention times of the unknown and N<sub>2</sub>O standard, shown in Figure 5, were identical.

With the identification of the stable gaseous products of radiolysis thus accomplished, the dependence of their formation on dose was determined. After radiolysis, samples were thermally equilibrated prior to analysis. Figure 6 shows this dependence to be linear from 15 to 60 megarads, with corresponding constant G values calculated from the slope of each linear portion of the curve. Apparent induction periods exist for oxygen and for nitrogen, but not for nitrous oxide. This implies that the mechanism of N<sub>2</sub>O formation is independent of those of O<sub>2</sub> and N<sub>2</sub> formation.

TABLE 10  
Mass Spectrometric (M/e) Fragmentation of N<sub>2</sub>O and  
CO<sub>2</sub> Standards

Standard	M/e Species					
CO <sub>2</sub>	44/CO <sub>2</sub> <sup>+</sup>	-----	28/CO <sup>+</sup>	22/CO <sub>2</sub> <sup>++</sup>	16/O <sup>+</sup>	-----
N <sub>2</sub> O	44/N <sub>2</sub> O <sup>+</sup>	30/NO <sup>+</sup>	28/N <sub>2</sub> <sup>+</sup>	-----	16/O <sup>+</sup>	14/N <sup>+</sup>

TABLE 11  
Mass Spectrometric Analysis of Radiolytic  
Product Fractionated at -130°C

M/e Fractions	Intensity (Peak Height) Ratios of M/e Fractions				
	N <sub>2</sub> O Standard <sup>a</sup>	Experimental Determinations			
		1	2	3	4
30/28 = NO <sup>+</sup> /N <sub>2</sub>	2.65	2.60	2.25	2.39	2.62
30/14 = NO <sup>+</sup> /N <sup>+</sup>	5.53	5.48	5.15	5.45	5.51
14/16 = N <sup>+</sup> /O <sup>+</sup>	2.34	2.37	2.34	2.22	2.32
44/30 = N <sub>2</sub> O <sup>+</sup> /NO <sup>+</sup>	2.90	3.28	3.02	3.02	3.10

<sup>a</sup>Based on N<sub>2</sub>O → NO<sup>+</sup> + N<sub>2</sub><sup>+</sup> + O<sup>+</sup> + N<sup>+</sup> + N<sub>2</sub>O<sup>+</sup> mass spectrometric fragmentation



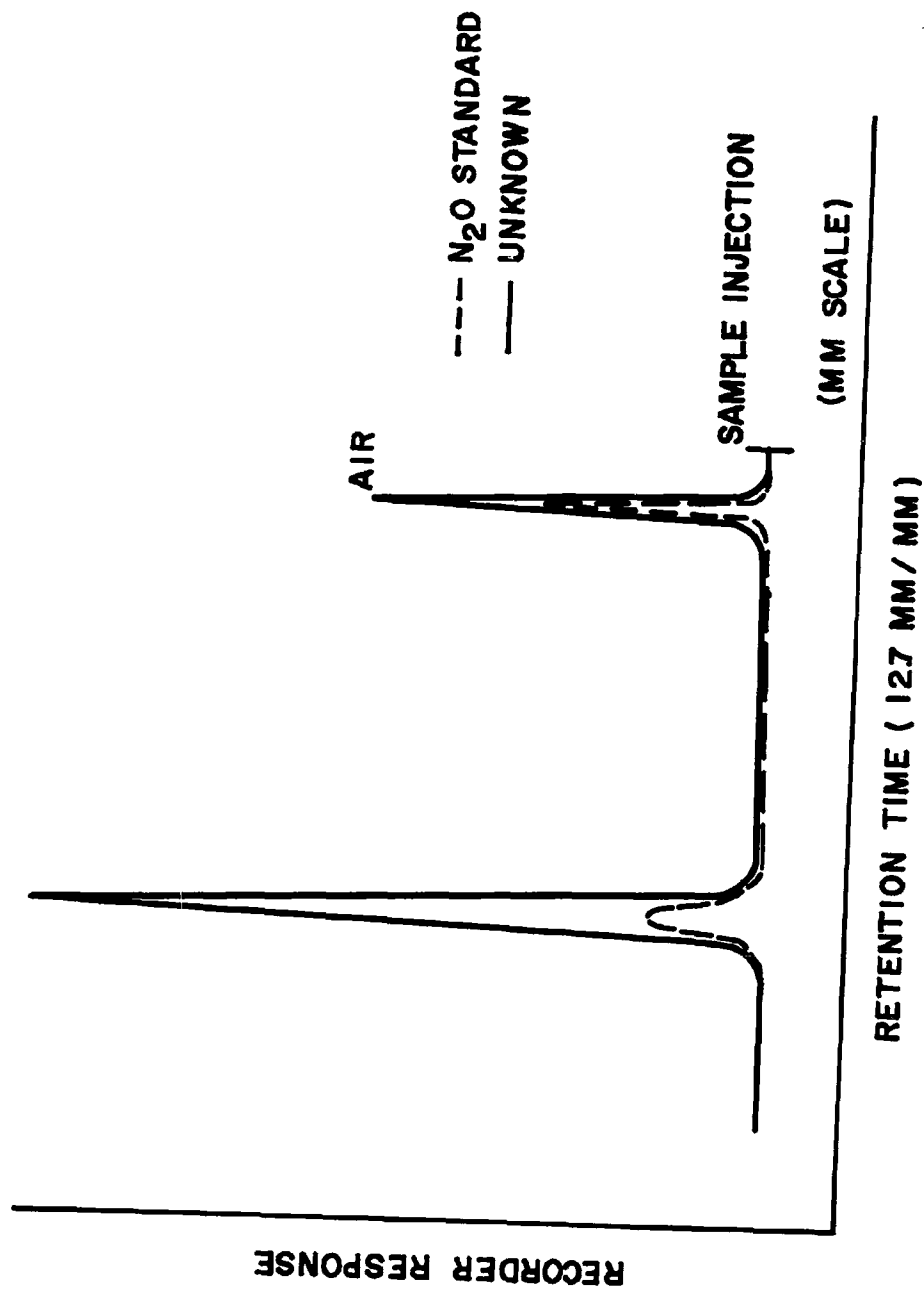


Figure 5. Vapor Phase Chromatogram Showing Relative Retention Times of Unknown and  $N_2O$  Standard

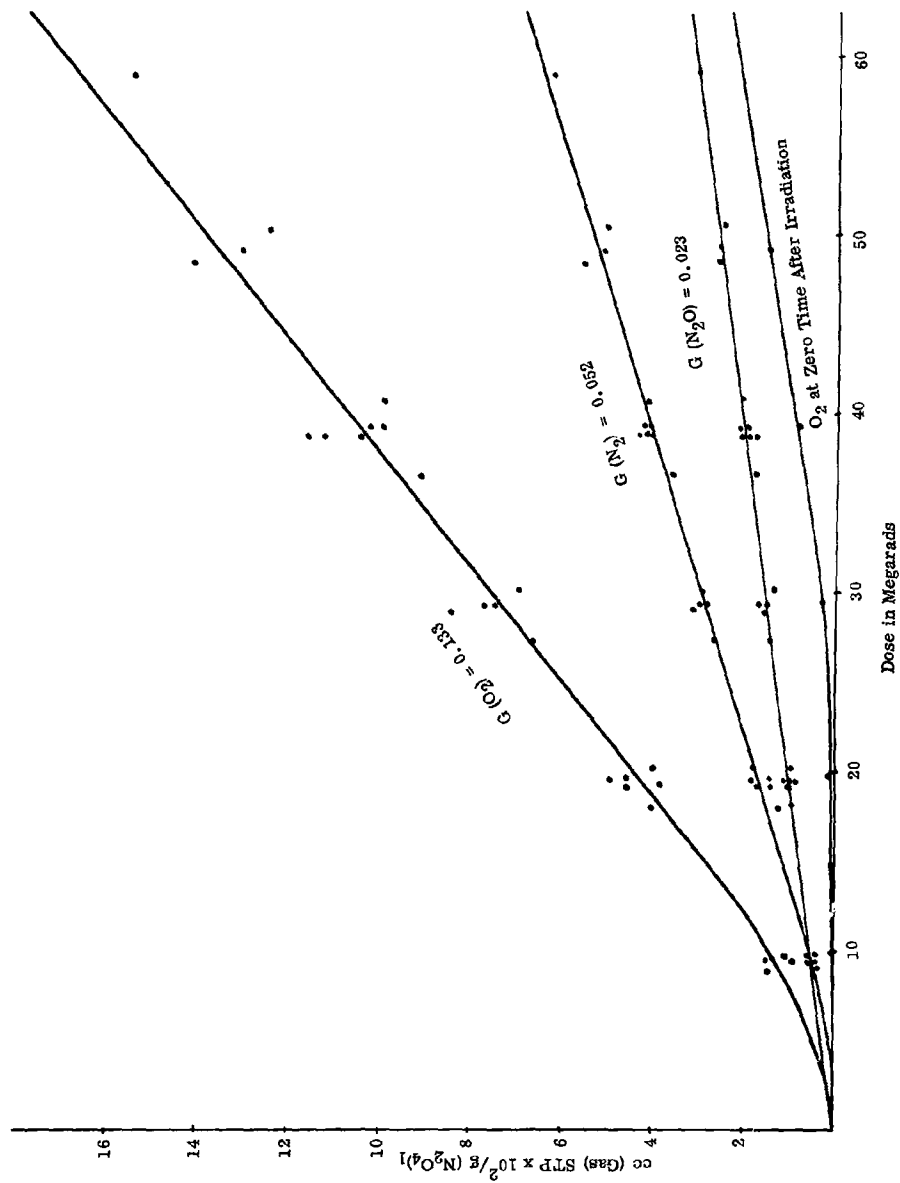
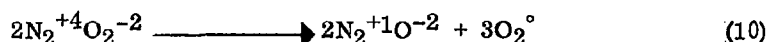
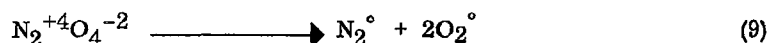


Figure 6. Cobalt-60 Gamma Radiolysis of Liquid  $\text{N}_2\text{O}_4$  at  $20^\circ\text{C}$ . Dependence of Isolated Gaseous Products on Dose (Dose Rate  $0.41 \text{ Mrad/hr}$ )

### Material Balance of Radiolytic Gaseous Products

Material balance calculations were based on the valence changes (i.e., changes in oxidation states) involved in the process of product formation according to the following equations:



For every  $\text{N}_2$  formed, there is a gain of 4 electrons per atom of nitrogen. In the formation of  $\text{N}_2\text{O}$ , there is a gain of 3 electrons per atom of nitrogen, and no change in electrons for the bound oxygen. Finally, there is a loss of two electrons per atom of oxygen per  $\text{O}_2$  produced. Multiplying the radiolytic yields of gaseous products by their respective valence changes,

$$4 [\text{N}_2] + 3 [\text{N}_2\text{O}] - 2 [\text{O}_2] = 0 \quad (11)$$

$$\text{or} \quad 2 [\text{N}_2] + 1.5 [\text{N}_2\text{O}] = [\text{O}_2] \quad (12)$$

gives an evaluation of the material balance obtained experimentally. These values are listed in Table 12 and show an average oxygen deficiency of  $2.3 \times 10^{-7}$  mole  $\text{O}_2$  per gram  $(\text{N}_2\text{O}_4)_1$  or  $2 \times 10^{-5}$  mole  $\text{O}_2$  per mole  $(\text{N}_2\text{O}_4)_1$ . The total observed decomposition of  $(\text{N}_2\text{O}_4)_1$  based on

$$G(\text{N}_2\text{O}_4) = G(\text{N}_2) + G(\text{N}_2\text{O}) \quad (13)$$

being  $G(\text{N}_2\text{O}_4) = 0.052 + 0.023 = 0.075$ .

### Radiolysis of $(\text{N}_2\text{O}_4)_1$ . Preparations, Including $\text{N}_2$ Sparging

It was considered possible that the oxygen used in the purification of  $(\text{N}_2\text{O}_4)_1$ , being entrained, was responsible for the formation of  $\text{N}_2\text{O}_5$  during radiolysis. To check this, samples which had been sparged with  $\text{N}_2$  after the usual sparging with  $\text{O}_2$  were irradiated and studied for post-irradiation rate of oxygen evolution and dependence of product formation on dose in the manner as described in previous experiments. The amount of oxygen evolved at  $20^\circ \pm 0.05^\circ \text{C}$  was observed to increase with each successive sample analysis performed in time as shown in Table 13.

TABLE 12

Material Balance<sup>a</sup> of Isolated Gaseous Products of  $(N_2O_4)_1$  Radiolysis

Expt. No	cc (Gas) STP $\times 10^2 / g(N_2O_4)_1$			$2N_2 + 1.5N_2O$ (A)	A - $O_2$	Dose Mr
	$O_2$	$N_2$	$N_2O$			
1-18-6	0.92	0.35	0.47	1.41	0.49	9.84
1-25-3	1.45	0.57	0.45	1.82	0.37	9.84
1-18-1	4.59	1.82	1.03	5.18	0.59	19.68
1-25-2	4.94	1.37	1.03	4.29	-0.65	19.68
1-18-2	7.70	2.91	1.62	8.25	0.55	29.52
1-25-1	7.50	2.83	1.62	8.09	0.39	29.52
11-30-4	9.87	4.08	2.00	11.16	1.29	40.70
1-18-3	10.25	4.04	2.11	11.25	1.00	39.36
1-18-5	9.90	4.12	1.90	11.09	1.19	39.36
1-18-4	12.96	5.04	2.50	12.96	0.87	49.20
12-14-4	12.42	4.95	2.42	13.52	1.10	50.45
1-25-4	15.34	6.11	2.96	16.66	1.32	59.04
7-4-5	11.55	4.38	1.70	11.31	-0.24	38.88
6-6-1	1.42	0.53	0.53	1.86	0.44	9.72
6-6-2	3.82	1.39	0.98	4.25	0.43	19.44
6-6-3	8.46	3.12	1.58	8.61	0.15	29.16
6-6-4	10.41	4.15	1.96	11.24	0.83	38.88
6-6-5	11.20	4.24	1.96	11.41	0.21	38.88
6-3-6	14.06	5.50	2.54	14.81	0.75	48.60
9-14-10	1.50	0.31	0.43	1.27	-0.23	9.17
9-14-8	4.00	1.20	0.91	3.77	-0.23	18.15
9-14-9	6.60	2.65	1.38	7.37	0.77	27.50
9-14-11	9.10	3.50	1.83	9.75	0.65	36.67
5-30-1	1.01	0.50	0.34	1.51	0.50	9.86
5-30-2	4.59	1.72	0.96	4.88	0.29	19.62
5-30-4	3.98	1.74	0.99	4.96	0.98	20.43
5-30-3	6.89	2.89	1.25	7.66	0.77	30.27
				Avg = 0.52		

<sup>a</sup>Based on  $O_2 = 2N_2 + 1.5N_2O$ 

$$\text{Mole } O_2 / g(N_2O_4)_1 \text{ Deficiency} = \frac{5.2 \times 10^{-3} \text{ cc/gm } N_2O_4 \times 10^{-3} \text{ mole}}{22.4 \text{ cc/m Mole}} =$$

$$2.3 \times 10^{-7} \text{ or } 2 \times 10^{-5} / \text{mole } (N_2O_4)_1$$

TABLE 13

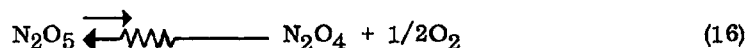
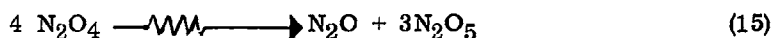
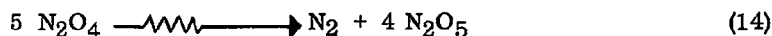
Post Irradiation Rate of  $\text{N}_2\text{O}_5$  Decomposition at  $20^\circ\text{C} \pm 0.05^\circ$ 

Grams ( $\text{N}_2\text{O}_4$ ) <sub>1</sub>	mm Gas ( $\text{N}_2 + \text{O}_2$ )	( ( $\text{N}_2\text{O}_4$ ) <sub>1</sub> purification included $\text{N}_2$ sparging)			Fraction $\text{N}_2\text{O}_5$ Remaining	Seconds ( $\times 10^{-4}$ )	Spec. Rate Const. ( $\times 10^4 \text{ sec}^{-1}$ )
		Percent $\text{O}_2$	$^\circ\text{K}$	cc ( $\text{O}_2$ ) STP gm ( $\text{N}_2\text{O}_4$ ) <sub>1</sub> ( $\times 10^2$ )			
5.800	113.7	38.9	295.2	2.80	0.758	0	—
5.780	161.0	56.9	296.0	5.83	0.518	2.88	0.13
5.690	182.5	62.4	297.0	7.31	0.395	5.76	0.11
5.730	195.8	64.1	296.5	8.01	0.306	8.64	0.10
5.581	207.2	66.6	295.0	9.98	0.136	17.46	0.10
5.632	244.0	72.5	294.5	11.55	0	—	—
Average 0.11							—

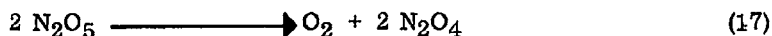
The fractions of  $\text{N}_2\text{O}_5$  corresponding to these amounts were used to calculate the specific rate constants. The average rate constant is in excellent agreement with those obtained from samples sparged with oxygen only. Figure 7 shows the curves for these comparable determinations to be superposable. Further comparisons of the effect of  $\text{N}_2$  sparging with respect to the dependence of product formation on dose are shown in Figures 8 and 9. In all cases, the slopes of the curves are identical. These results indicate that the use of  $\text{O}_2$  in purifying  $(\text{N}_2\text{O}_4)_1$  is not in any way responsible for the formation of  $\text{N}_2\text{O}_5$  during radiolysis.

#### Radiolysis of $(\text{N}_2\text{O}_4)_1/\text{O}_2$

On the basis of studies of the decomposition of  $\text{N}_2\text{O}_5$  during and after radiation, it appeared that the oxygen given off in the radiolysis of  $(\text{N}_2\text{O}_4)_1$  to  $\text{N}_2$  and  $\text{N}_2\text{O}$  combines with  $\text{N}_2\text{O}_4$  to form  $\text{N}_2\text{O}_5$ . During radiolysis, the  $\text{N}_2\text{O}_5$  was shown to be stabilized in a gamma field. After radiolysis, however, it decomposes following the first order kinetics reported in the literature but at a slightly slower rate because of the prevailing dilution factor. These processes can be represented by the following set of equations:



and at thermal equilibrium,



If this were indeed the mechanism of oxygen consumption and subsequent release after radiolysis, certainly any addition of oxygen to  $(\text{N}_2\text{O}_4)_1$  would behave in the same manner. To establish the validity of this postulate, irradiation studies were conducted with known quantities of  $\text{O}_2$  added to  $(\text{N}_2\text{O}_4)_1$ .

Double break seals, which facilitated the introduction of  $\text{O}_2$  to  $(\text{N}_2\text{O}_4)_1$  and subsequent degassing of products after radiolysis, were calibrated and the volume of gases was determined by the calculations shown in Table 14.

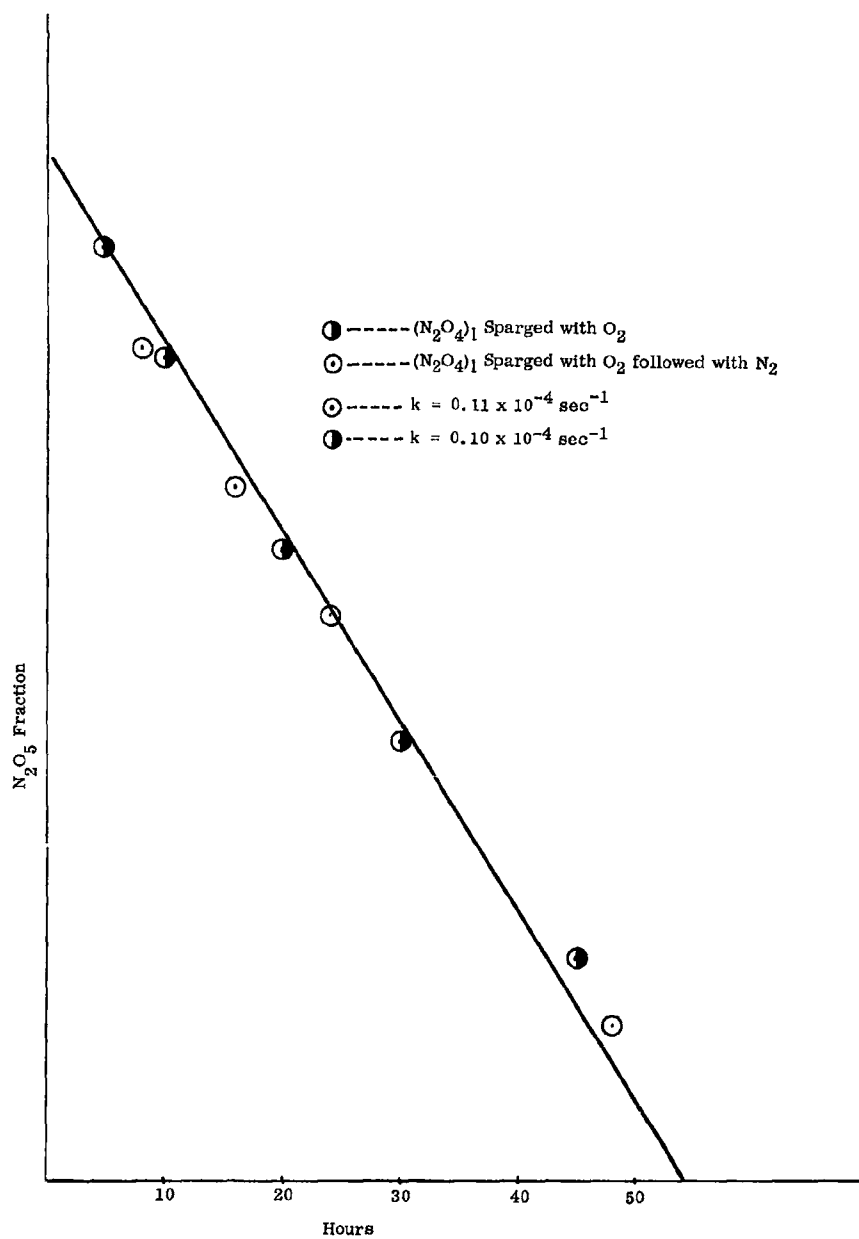


Figure 7. Dependence of Post Irradiation Rate of  $\text{N}_2\text{O}_5$  Decomposition at  $20^\circ\text{C}$  On Variation in  $(\text{N}_2\text{O}_4)_1$  Purification Procedure

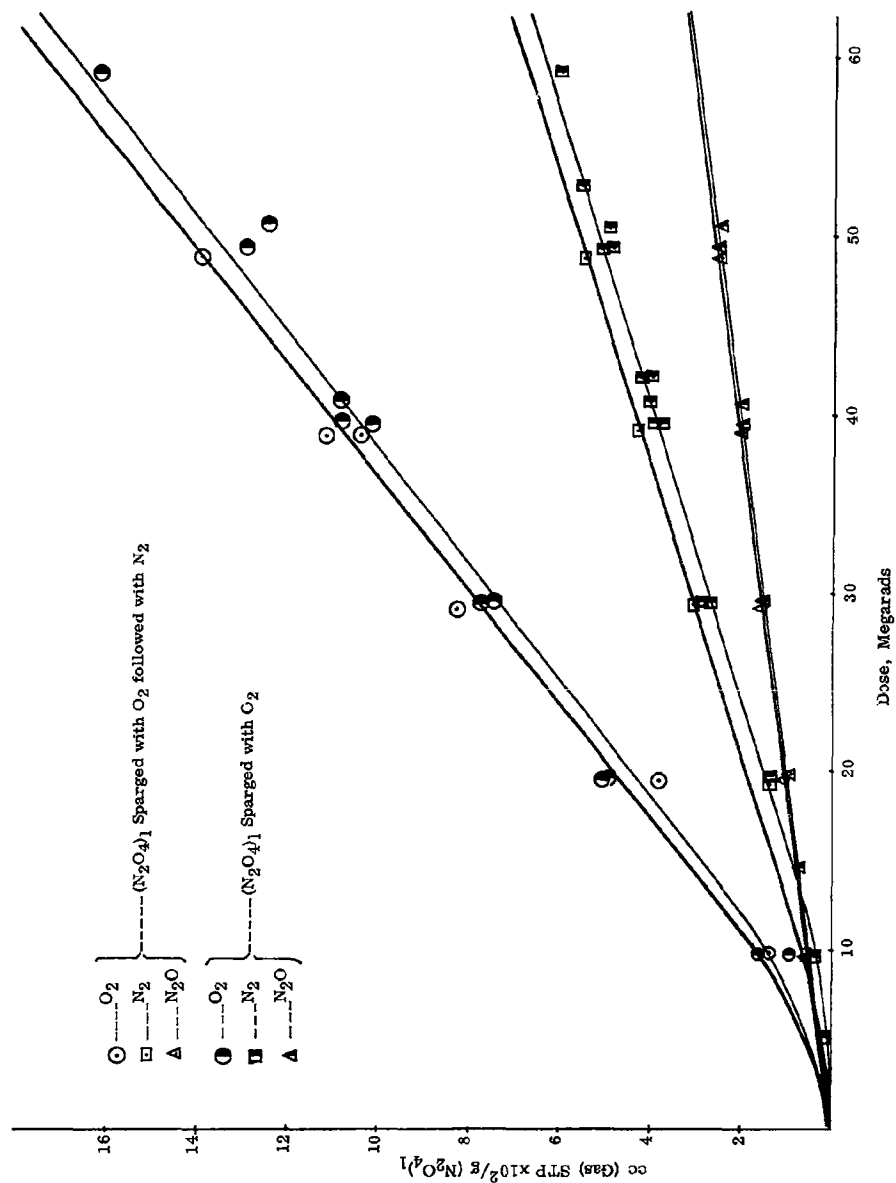


Figure 8. Effect of Variation in  $(N_2O_4)_1$  Purification Procedure on Dependency of Yields of Products on Dose



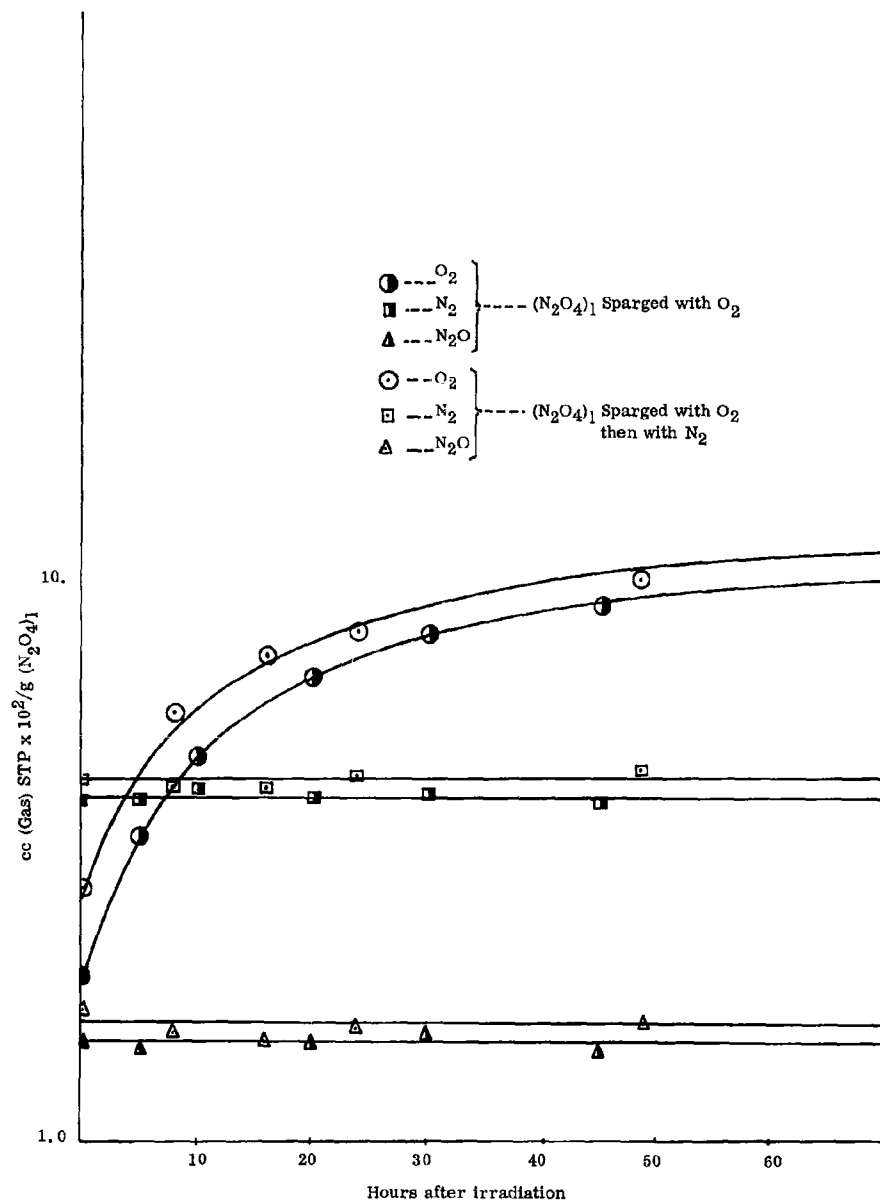


Figure 9. Dependence of Post Irradiation Rates of Gaseous Products Formation at 20°C On Variation in  $(N_2O_4)_1$  Purification Procedure

TABLE 14

Quantities and Partial Pressures<sup>b</sup> of O<sub>2</sub> in Free Space Above (N<sub>2</sub>O<sub>4</sub>)<sub>l</sub> in Sealed Ampoules

Expt. No.	Break-Seal Vol (cc) <sup>a</sup> (V <sub>1</sub> )	mm (O <sub>2</sub> ) Break-Seal Pres (P <sub>1</sub> )	°K	cc (O <sub>2</sub> ) STP	Ampoule Vol. (cc)	Total Vol. (Amp. + V <sub>1</sub> )	(N <sub>2</sub> O <sub>4</sub> ) <sub>l</sub> Vol. (cc)	Free Space (V <sub>2</sub> )	P.P. (O <sub>2</sub> ) Above (N <sub>2</sub> O <sub>4</sub> ) <sub>l</sub> P <sub>1</sub> x V <sub>1</sub> /V <sub>2</sub> = P <sub>2</sub>
8-31-3	1.666	546.0	295.2	1.106	3.46	5.13	2.82	2.31	394
8-31-11	1.887	518.0	294.5	1.192	4.45	6.34	3.53	2.81	348
8-31-10	1.853	518.0	294.5	1.170	4.18	6.03	3.29	2.74	350
8-31-12	1.826	546.0	295.2	1.215	4.23	6.06	3.21	2.85	350
9-7-5	1.792	304.5	293.7	0.668	4.43	6.22	3.63	2.59	210
9-7-1	1.813	304.0	295.5	0.670	4.53	6.34	3.48	2.86	193
9-7-3	1.847	304.5	295.4	0.684	4.26	6.11	3.84	2.27	248
9-7-2	1.905	304.0	295.5	0.706	4.28	6.19	3.22	2.97	196

<sup>a</sup> Corrected for density of water at temperature determinations were made, viz; 0.99765g/cc at 22.5° C<sup>b</sup> Uncorrected for solubility of O<sub>2</sub> in (N<sub>2</sub>O<sub>4</sub>)<sub>l</sub>

The corresponding partial pressures of  $O_2$  above the  $(N_2O_4)_1$  are also included in Table 14. As a check on the technique of  $O_2$  addition calculated quantities were compared to those obtained from analyses both in the presence and absence of  $(N_2O_4)_1$ . These results, given in Table 15, are shown to be in very good agreement. Directly after irradiation at various doses the samples were quenched in a dry-ice bath and analyzed in the usual manner for  $N_2$ ,  $O_2$ , and  $N_2O$  content. This period of analyses was designated "zero time after irradiation." The samples were then resealed and analyzed for gaseous product formation after thermal equilibration (attained by storage at  $25^\circ C$  for 7 days). The gases isolated at zero time were  $N_2$ ,  $O_2$ , and  $N_2O$  and, at thermal equilibrium, only  $O_2$  was present, as is shown mass spectrometrically.

The relationship of these product analyses to the material balance calculations shown in Table 16 was based in part on Equation 12, which is derived from the valence changes involved in product formation. An equivalent method of arriving at this material balance formula is by use of Equations 14, 15, and 17, where the products at thermal equilibrium are equated to the total concentration of  $N_2O_5$ , i. e.,  $N_2 \sim 4 N_2O_5$ ;  $N_2O \sim 3 N_2O_5$ ; and  $O_2 \sim 2 N_2O_5$ . Therefore, the total concentration of  $N_2O_5$  at thermal equilibrium (th. eq.) is given by

$$2 (O_2)_{th. eq.} = (N_2O_5) = 4 N_2 + 3 N_2O \quad (18)$$

However, to account for the oxygen added in these experiments, the quantity of  $O_2$  determined at time zero,  $(O_2)_t$ , is subtracted from the quantity added initially,  $(O_2)_o$ , and the difference is added to Equation 18.

$$2 (O_2)_{th. eq.} = (N_2O_5) = 4 N_2 + 3 N_2O + 2 [(O_2)_o - (O_2)_t] \quad (19)$$

$$\text{or} \quad (O_2)_{th. eq.} = (N_2O_5)/2 = 2 N_2 + 1.5 N_2O + [(O_2)_o - (O_2)_t] \quad (20)$$

By the use of Equation 20, the material balance obtained in this set of experiments was found to be good to within  $\pm 8\%$ .

Plots of the volumes of  $N_2$  and  $O_2$  determined at zero time after irradiation and the volume of  $O_2$  at thermal equilibrium versus dose in megarads are given in Figure 10. These determinations were made at partial pressures of  $O_2$  ranging from 200 to 350 mm (see Table 21). The induction period for  $N_2$  formation appears to have been eliminated

TABLE 15  
Quantitative Determination of Gas Added to  $(N_2O_4)_1$

2 4 1

Calculated		Experimental					
Gas <sup>a</sup>	Break Seal Pres (mm)	°K	Break Seal Vol (cc)	cc (Gas) STP	mm (Gas)	°K	cc (Gas) STP
O <sub>2</sub>	301.2	295.4	2.055	0.753	198	294.4	0.728
O <sub>2</sub>	253.0	293.7	1.858	0.575	158	294.3	0.582
O <sub>2</sub>	253.0	295.3	1.629	0.503	137	295.3	0.502
O <sub>2</sub>	301.2	293.7	1.771	0.653	183	294.8	0.672
Ar	574.0	295.8	1.726	1.204	330	297.1	1.203
Ar	574.0	295.8	1.782	1.254	338	294.6	1.243
N <sub>2</sub> <sup>b</sup>	375.5	295.4	1.743	0.796	220	297.0	0.802
N <sub>2</sub>	375.5	295.4	1.737	0.793	219	296.5	0.800

<sup>a</sup>Gases scrubbed with activated charcoal in an appropriate refrigerant and mass spectrometric analyses showed their purity to be > 99%

<sup>b</sup>Determination made in the absence of  $(N_2O_4)_1$

TABLE 16

Material Balance of Gaseous Products of  $(N_2O_4)_1/O_2$  Radiolysis

Expt. a No.	$(N_2O_4)_1$ Wt. (grams)	P. P. $(O_2)$ STP in Free Space (mm)	cc $(O_2)$ STP Added Initially (C)	cc (Gas) STP At Zero Time After Irradn		cc $(O_2)$ STP At Thermal Equilibrium <sup>a</sup> (E)	cc (Gas) STP/g $(N_2O_4)_1$		$2A + \frac{3}{2}B + C - D$	$\Delta$ (E-X)
				$N_2$ (A)	$N_2O$ (B)	$O_2$ (D)	$N_2$	$N_2O$		
8-31-3	4.082	394	1.106	0.098	0.017	0.674	0.009	0.004	0.114	-0.087
8-31-11	5.100	343	1.192	0.094	0.044	0.842	0.018	0.009	0.119	0.004
8-31-10	4.780	350	1.170	0.132	0.070	0.938	0.028	0.015	0.129	0.013
8-31-12	4.650	350	1.215	0.185	0.088	1.097	0.040	0.019	0.133	-0.002
9-7-5	5.265	210	0.668	0.043	0.024	0.320	0.009	0.005	0.109	0.095
9-7-1	5.040	193	0.670	0.092	0.043	0.386	0.018	0.009	0.122	0.085
9-7-3	5.570	243	0.684	0.165	0.077	0.433	0.030	0.014	0.124	0.056
9-7-2	4.670	196	0.706	0.133	0.037	0.646	0.041	0.019	0.135	0.055

<sup>a</sup> Source intensity 0.382 Mrad/hr.<sup>b</sup>  $O_2$  evolved after 7 days at 25°C

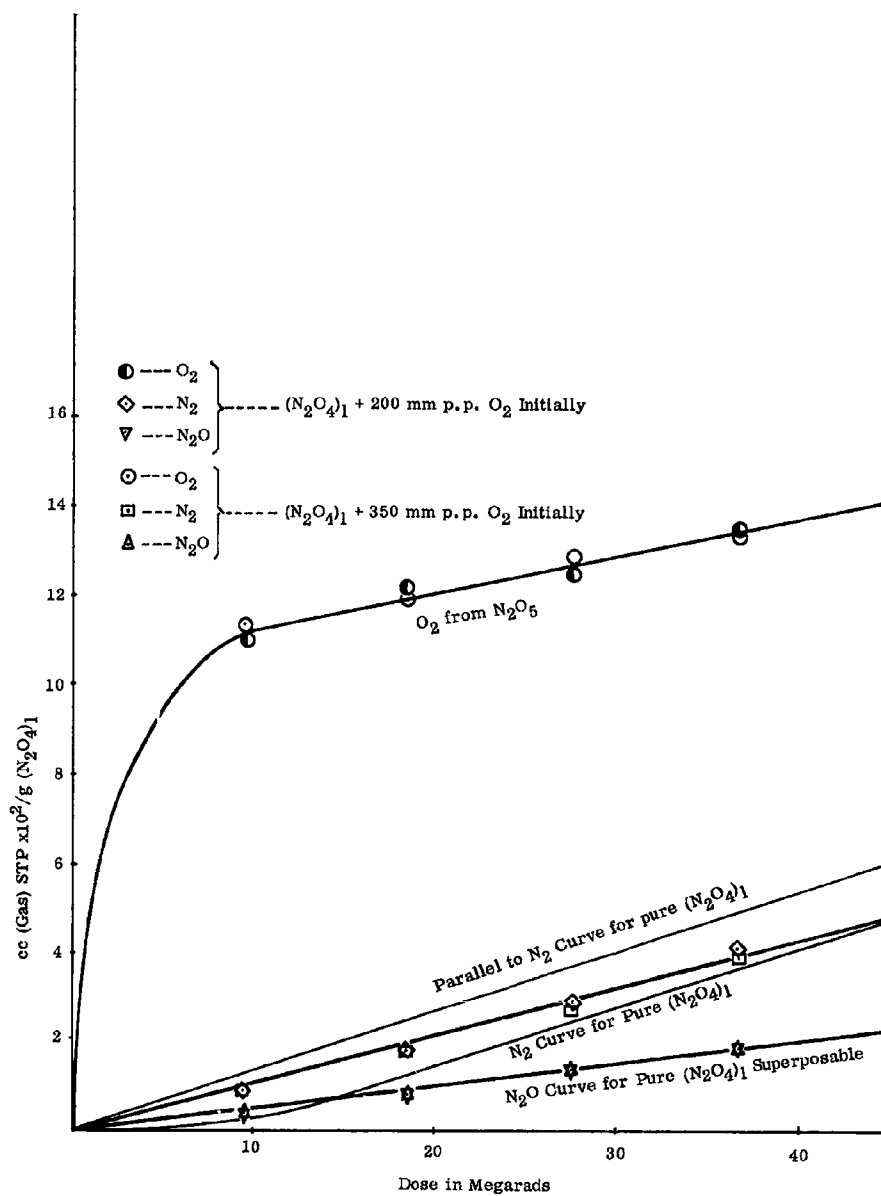


Figure 10. Cobalt-60 Gamma Radiolysis of Liquid N<sub>2</sub>O<sub>4</sub> at 20°C.  
Effect of Adding Oxygen on Dependence of Gaseous Products  
Formation on Dose (Dose rate: 0.382 Mrad/hr)

by the addition of oxygen. This may indicate that  $O_2$  is involved in the formation of  $N_2$ , increasing the concentration of precursors to their steady state proportions. Although the slope for  $N_2$  is less, that of  $N_2O$  is superposable on the curves obtained for pure  $(N_2O_4)_1$ . Consistent with the premises made initially for this series of experiments, the rate of  $O_2$  evolution is equivalent to the rate of  $N_2O_5$  formation, which should be the same for the pure  $(N_2O_4)_1$  as for the  $(N_2O_4)_1$  containing  $O_2$ . From the slopes of the  $O_2$  curves obtained in Figures 10 and 6, the latter including a curve for  $O_2$  at zero time in the case of pure  $(N_2O_4)_1$ , the  $G(N_2O_5)$  formation corresponding to their respective rates of formation was calculated and found to be in excellent agreement.

$$G(N_2O_5)_{\text{pure } (N_2O_4)_1} = 1.11 \text{ and } G(N_2O_5)_{(N_2O_4)_1 + O_2} = 1.12$$

(The calculations are given in the appendix of this report.) This, then, unequivocally establishes the formation of  $N_2O_5$  via the combination with the oxygen present, whether added initially or, as a product of radiolysis, formed during irradiation.

#### Radiolysis of $(N_2O_4)_1/Ar$

The noble gases are often added to systems under investigation in radiation studies for the more efficient absorption of photon energy via a charge-transfer mechanism. The inert gases act as energy sinks, as do catalysts, effectively transferring the incident energy to the system being radiolyzed. To investigate this effect, known quantities of argon were added to  $(N_2O_4)_1$  in the manner outlined for the  $O_2$  additions, subjected to various doses, and analyzed for product formation. The gases isolated at thermal equilibrium were the same and in identical proportions as those obtained from the radiolysis of pure  $(N_2O_4)_1$ . These results, summarized in Figure 11, show the dependence of product formation on dose for all three gases to be linear from 15 to 40 megarads, with slopes superposable on those obtained for pure  $(N_2O_4)_1$ . The fact that the presence of argon had no effect on the yields of the products of radiolysis can be attributed to the apparent insolubility of argon in  $(N_2O_4)_1$ .

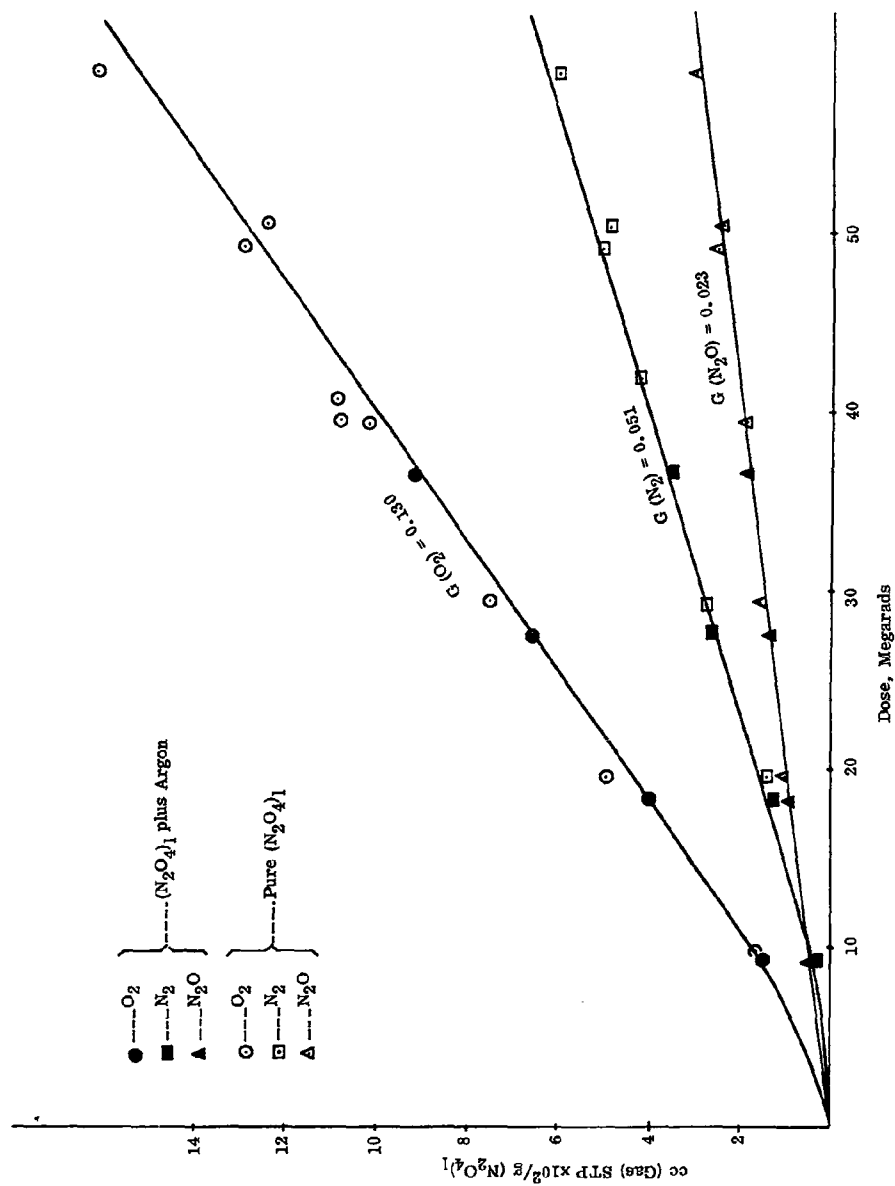
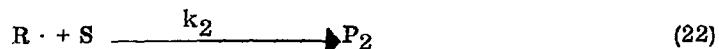
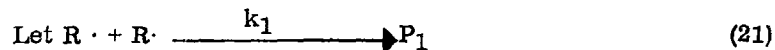


Figure 11. Effect of Argon on Dependence of Yields of Products on Dose



# Effect of Dose Rate on Radiolysis of $(N_2O_4)_1$

The dependence of product formation on the intensity of a gamma field is given by the following relationships:

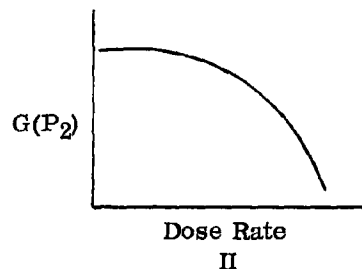
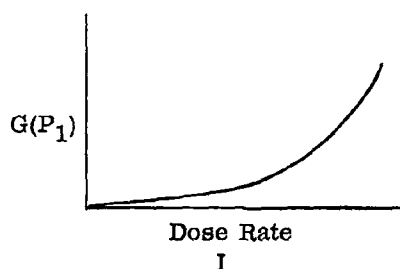


where S = molecule;  $R \cdot$  = radical.

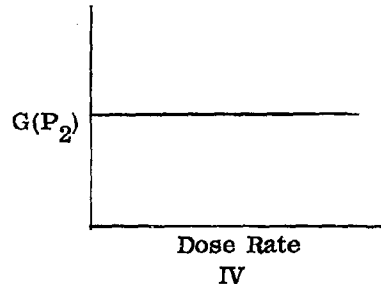
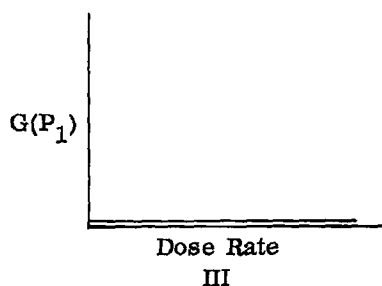
Then,

$$\frac{k_1(R \cdot)}{k_2(S)} = \frac{k_1(R \cdot)^2}{k_2(S)(R)} \quad (23)$$

It is seen from Equation 23 that the rate of radical-radical combination is dependent on the square of the concentration. Since the concentration of such reactive species is a function of source intensity, processes involving competing  $R \cdot + R \cdot$  and  $R \cdot + S$  combinations would be affected by variations in intensities of incident radiations. This effect would result in the following types of curves:



For those events involving only  $R \cdot + S$  but no  $R \cdot + R \cdot$  reactions, the expected curves would be:



To determine the effect of the intensity of radiation on the formation of products, samples were irradiated with a cobalt-60 source having one-thirtieth the intensity of the source normally used in this study. Samples were irradiated as a function of dose, and analyzed for product formation after thermal equilibration. Figure 12 shows that the radiation dose has no effect on product formation, since the curves obtained are superposable on those derived from irradiations with the normally more intense source. When G values calculated from the linear portions of these curves are plotted against dose rate, it is obvious that the resulting curve will be type IV. This indicates that the processes taking place during irradiation are not of the radical-radical type but rather of the radical-molecule type. With establishment of the independence of product formation in relation to changes in the intensity of incident radiation, it became possible to study the induction period more accurately using a low intensity source. Figure 13 shows the induction part of the curve to be real in that straight lines for  $O_2$  and  $N_2$  formation could not possibly be drawn through the origin but must intercept the X axis. At the same time the linear curve for  $N_2O$  is equally established as passing through the origin and found to be independent of source strength.

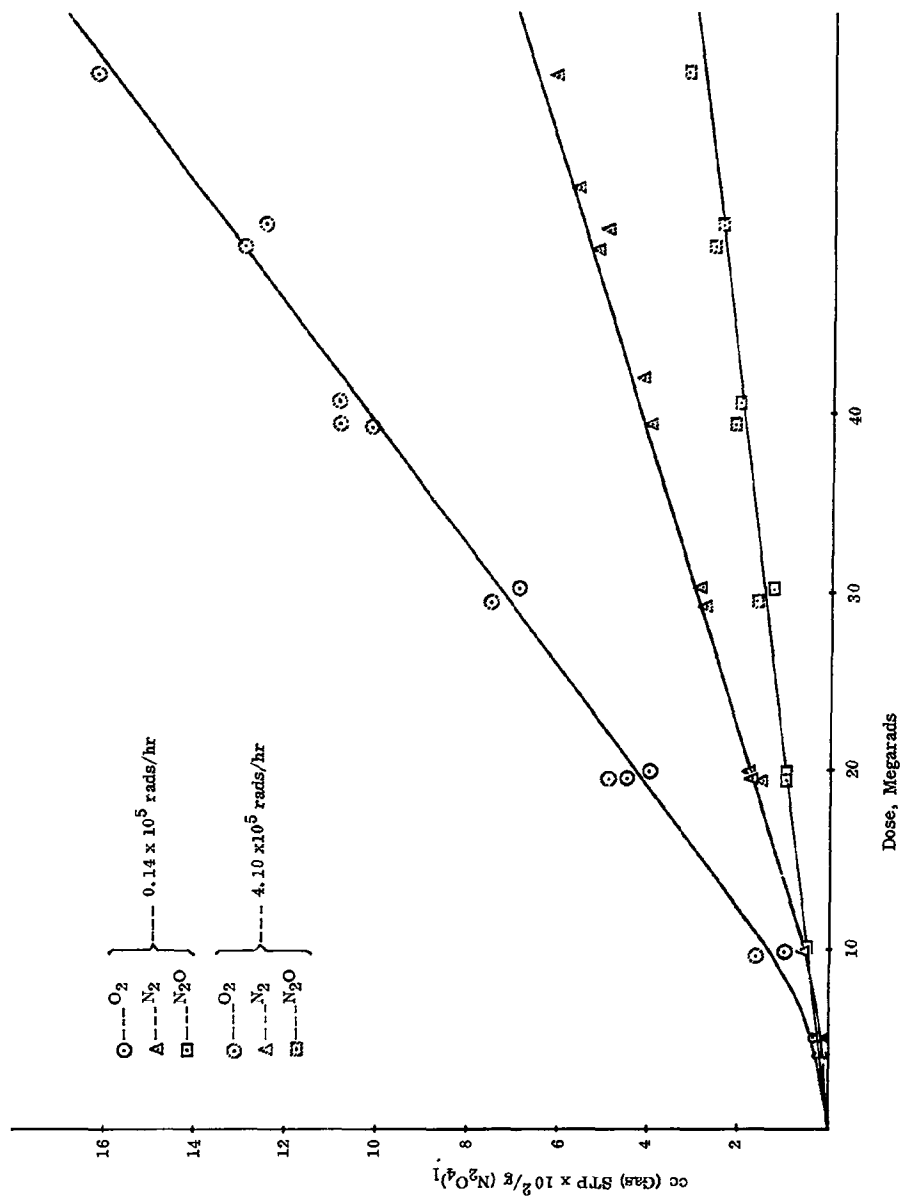


Figure 12 Dependence of Gaseous Products Formation During Radiolysis on Dose at Different Rates

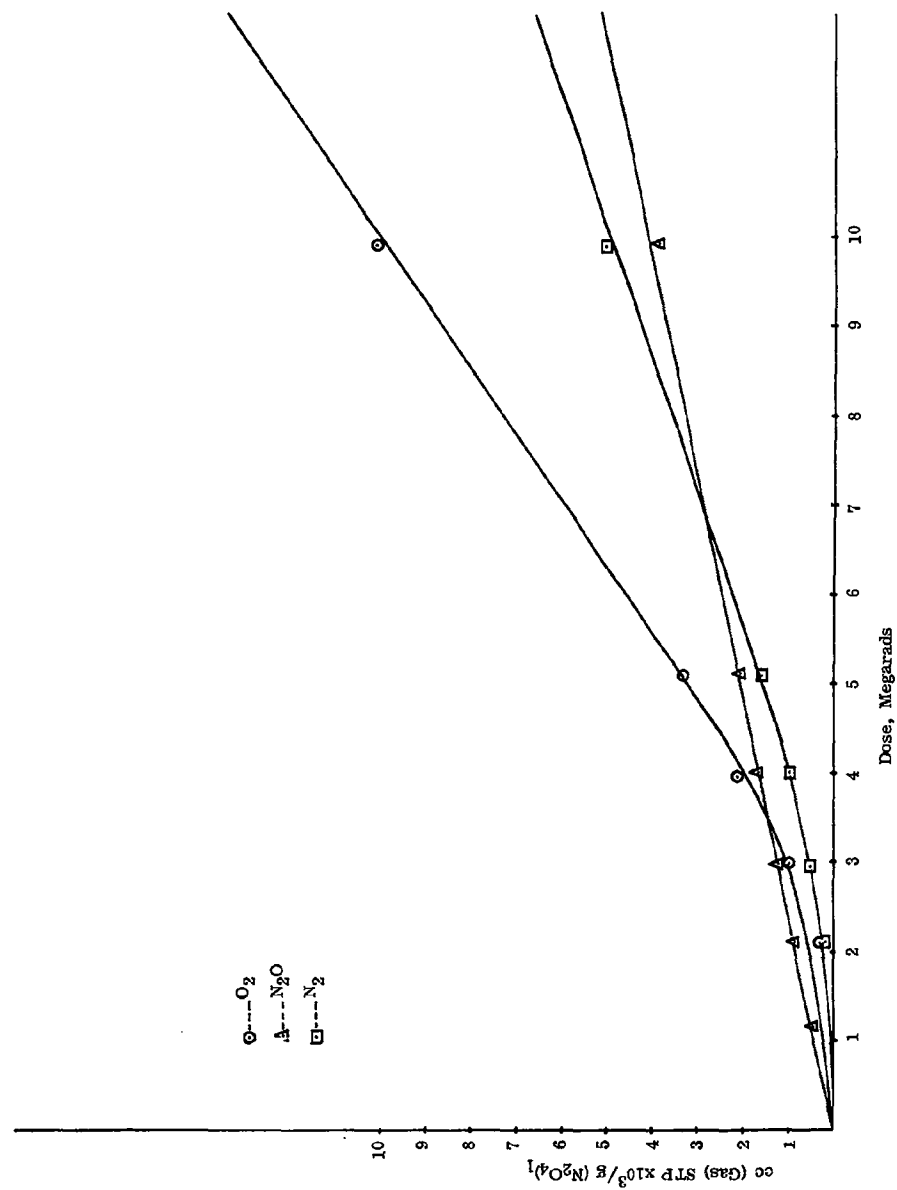


Figure 13. Cobalt-60 Radiolysis of  $(N_2O_4)_I$  at  $20^\circ C$ ; Dependence of  $G(O_2)$ ,  $G(N_2O)$ , and  $G(N_2)$  on Dose (Source Intensity  $1.37 \times 10^{14} r/hr$ )

## EXPERIMENTAL PROCEDURES

### Purification of $(\text{N}_2\text{O}_4)_1$

Tank gas (99% pure) was liquefied in approximately 40 cc aliquots and sparged with oxygen purified by passage over hot CuO and through a dry-ice trap. The  $(\text{N}_2\text{O}_4)_1$  was distilled twice through phosphorus pentoxide-saturated glass wool and degassed two times at  $-78^\circ\text{C}$ . (The glass wool used in this manner was treated with mixed  $\text{HNO}_3/\text{H}_2\text{SO}_4$  acids and washed repeatedly with boiling distilled water until neutral to blue litmus and dried several days in an oven set at  $110^\circ\text{C}$ .) The  $(\text{N}_2\text{O}_4)_1$  was then transferred to that part of the vacuum line protected from grease by glass bead traps and degassed a third time at  $-78^\circ\text{C}$ . Only the center cut was distilled into 5 cc pyrex break seals for irradiation studies. Kel-F grease (chlorotrifluoropolyethylene) which was found to be inert to  $\text{NO}_2$  was used on all standard joints and stop-cocks. (See Figure 14 for details of apparatus.)

### Gas Analyses

After radiolysis, the samples were degassed at  $-196^\circ\text{C}$  and the  $\text{N}_2/\text{O}_2$  gas mixture was toeplered into the McLeod gauge end of the vacuum line. The total quantity of gas was determined in the manner usually employed in vacuum techniques. Aliquots were reserved for mass spectrometric check analyses and the remainder was analyzed by the platinum filament combustion method. Approximately 5 microns of the unknown mixture was used for each determination, designated  $P_I$ . An estimated excess of  $\text{H}_2$  (Purified and checked mass spectrometrically to have a purity of better than 99%) equivalent to  $P_I$  assumed to be 100%  $\text{O}_2$  was added to  $P_I$  and the total pressure denoted as  $P_T$ . The platinum filament was then heated to the barely perceptible glow point and the water of combustion was removed by means of a cold finger at  $-196^\circ\text{C}$ . The combustion was considered complete when pressure readings became constant. The residual gas pressure at the end of combustion was termed  $P_R$ . Then,

$$\frac{P_T - P_R}{3P_I} \times 100 = \% \text{O}_2.$$

Mass spectrometric check analyses of  $\text{N}_2/\text{O}_2$  were calculated from the relative mass peak heights and corrected for the respective peak height sensitivity response differences of the recording instrument, e. g. ,

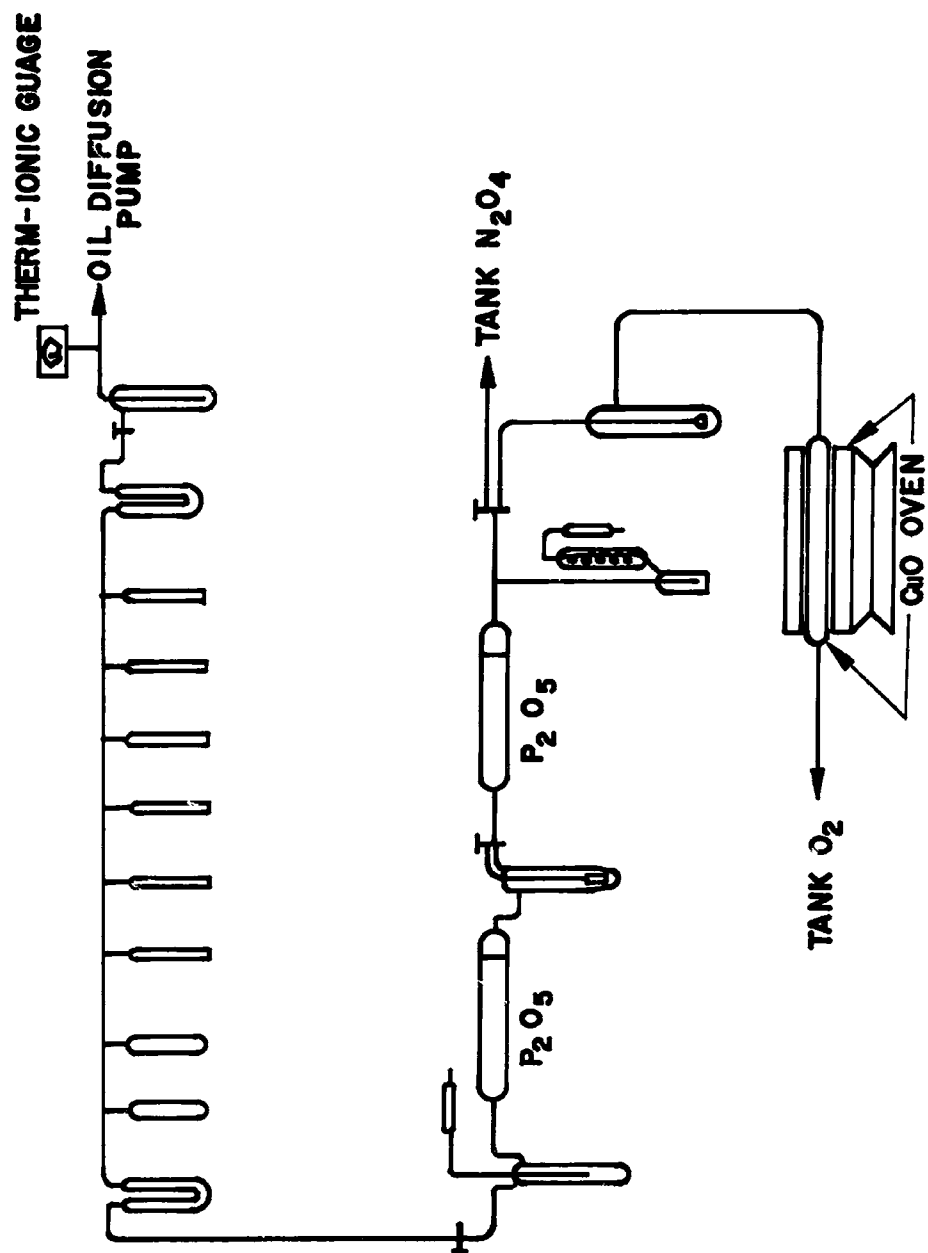


Figure 14 Apparatus for  $(\text{N}_2\text{O}_4)_1$  Purification and Sample Preparation

sensitivity for  $O_2$  = 344.2 divisions of peak height per mm pressure and 395.0 divisions per mm pressure for  $N_2$ . (See Figure 15 for details of apparatus.)

$N_2O$  was isolated at  $-130^\circ C$  using a 2-chlorobutane-liquid nitrogen bath directly after degassing irradiated samples at  $-196^\circ C$ . The gas was then transferred to a cold finger and degassed at  $-196^\circ C$  prior to final pressure readings.  $N_2O$  was identified mass spectrometrically and checked by vapor phase chromatographic analysis using standard reference samples in each method of analysis. A GC-2 instrument equipped with a 4-foot silica gel (70010) column heated to  $40^\circ C$  was used in the check analysis.

#### Preparation of Synthetic Solutions of $N_2O_5$ in $(N_2O_4)_1$

$(N_2O_4)_1$  purified in the manner outlined above was transferred under vacuum to a specially designed bubbler adaptable to a commercially available ozonizer apparatus. Before exposing the  $(N_2O_4)_1$  to atmospheric pressure the entire glassware apparatus of the ozonizer was flushed with dry oxygen. The oxygen was dried by passage through a  $P_2O_5$  tube, followed by a dry-ice trap. The outlet to the atmosphere was affixed with a drying tube filled with Drierite. After flushing for five minutes, the ozonizer was turned on and the  $(N_2O_4)_1$  sparged with the  $O_3/O_2$  mixture at a gentle fixed rate for 10 minutes. To minimize the loss of  $N_2O_4$ , the bubbler containing the  $(N_2O_4)_1$  was immersed in a brine-ice bath. The solution of  $N_2O_5$  in  $(N_2O_4)_1$  was then attached to the vacuum line and degassed twice at  $-78^\circ C$  and transferred to a set of six break-seal ampoules radially connected to a common tubing. The entire set of ampoules was immersed in a common dry-ice bath. By this arrangement, the ampoules were simultaneously and uniformly filled. Prior to flame sealing, the solutions were degassed a third time.

#### Oxygen and Argon Additions

A double break-seal of the type shown below was used for the addition of known quantities of oxygen and argon.

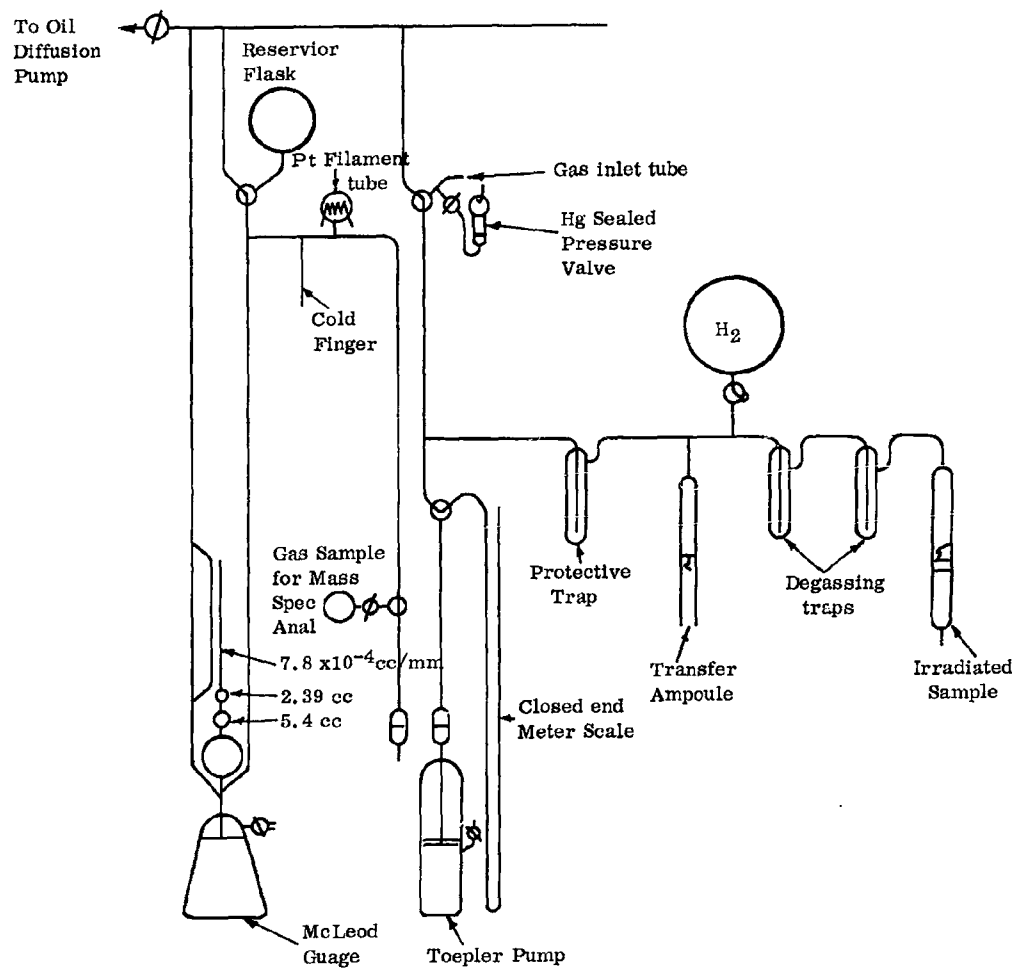
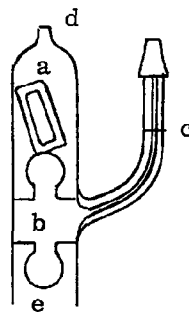


Figure 15. Vacuum Line for Gas Analyses

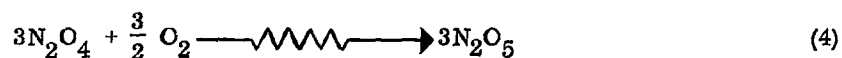
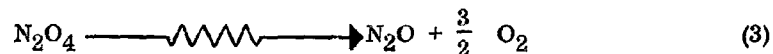
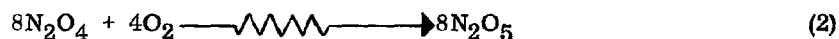
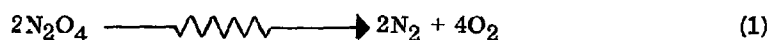




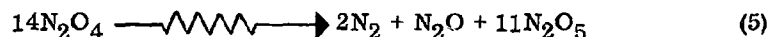
Volume b was calibrated by filling it to point c with water devoid of air bubbles. This was accomplished with a syringe affixed to a flexible stainless steel capillary tube inserted through the one millimeter bore side arm. The double break seal was attached to the vacuum line and either pure oxygen or argon (analyzed mass spectrometrically for purity) was introduced at pressures read on the meter scale. Using a small sharp flame, the side arm was rapidly sealed at the calibration line. Obtaining the volumes and pressures in this manner, the quantity of gas in the double break seal was accurately determined. The ampoule containing the glass encased hammer and a known quantity of gas was then attached to the sample preparation line. Pure  $(\text{N}_2\text{O}_4)_1$  was distilled into "a" in the manner described above and flame-sealed at "d". The end of the break seal in contact with the hammer was broken, allowing the gas to intermix with  $(\text{N}_2\text{O}_4)_1$ . After radiolysis, a second glass-encased hammer was inserted through end "e". The ampoule was then placed on the vacuum line (with "e" end up) and analyzed as usual.

## CONCLUSIONS

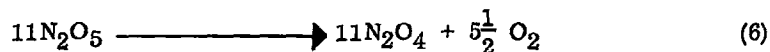
The products of cobalt-60 gamma radiolysis of liquid  $\text{N}_2\text{O}_4$  have been found to be  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{N}_2\text{O}_5$ . The processes involved in these product formations are of the radical-molecule type. After radiolysis, the oxygen evolved at thermal equilibrium, due to the decomposition of  $\text{N}_2\text{O}_5$  following first order kinetics, is in material balance with two parts of  $\text{N}_2$  to one of  $\text{N}_2\text{O}$ . The net mode of product formation has been shown to include the following steps and stoichiometric proportions:



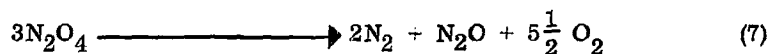
Addition of Equations 1 - 4 gives us



Then, at thermal equilibrium,



Subtracting (6) from (5) gives



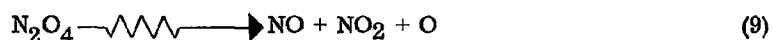
Initially, the radiation-induced reactions produce  $\text{O}_2$  or  $\text{N}_2\text{O}_5$ ,  $\text{N}_2\text{O}$ , and some precursor of  $\text{N}_2$ . The precursor is then converted to  $\text{N}_2$  by a process dependent on dose and therefore not thermally spontaneous. This is based on the experimental data showing the  $\text{N}_2$  buildup to be independent of dose rate and temperature. This means that during the induction period for  $\text{N}_2$ , in the 10-20 Mrad range, the precursor is stable in solution for 24 hours. The concentration of the precursor would be given by the negative intercept of the  $\text{N}_2$  curve, obtained from Figure 6, i. e.,

$$\frac{6.25 \times 10^{-3} \text{ cc(N}_2\text{)}/\text{g(N}_2\text{O}_4\text{)}}{2.24 \times 10^4 \text{ cc/mole}} = 2.9 \times 10^{-7} \text{ mole/g(N}_2\text{O}_4\text{)}$$

or  $2.9 \times 10^{-5}$  mole of precursor/mole  $\text{N}_2\text{O}_4$

When  $\text{O}_2$  is added, there is no intercept and it is therefore concluded that the excess  $\text{O}_2$  reacts with the precursor or an intermediate of the precursor to produce  $\text{N}_2$ . It must be emphasized that this reaction takes place only in the presence of an excess of  $\text{O}_2$ .

A possible mechanism for  $\text{N}_2$  production could be based on the formation of  $\text{N}_2\text{O}_3$  as the precursor, viz.

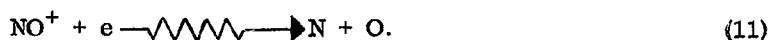


where  $\text{N}_2\text{O}_3 \rightleftharpoons \text{NO} + \text{NO}_2$

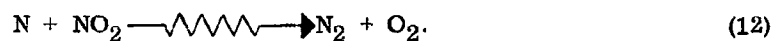
Since the ionization potential of  $\text{NO}$  is less than that of  $\text{NO}_2$ ,



and the charge is then transferred via



Finally,



In the presence of an excess of  $\text{O}_2$ , the reaction given in (9) is followed by,



In this manner, the steady state concentration of  $\text{N}_2\text{O}_3$  or  $(\text{NO} + \text{NO}_2)$  is attained instantaneously, and hence there is no induction period.

The extent to which these radical-molecule processes proceed to stable product formation has been shown to be in the order of 0.1 to

0.01 milli molar concentrations. Since the number of molecules of  $\text{N}_2\text{O}_4$  decomposing per 100 electron volts absorbed is only 0.075, it is quite obvious that  $(\text{N}_2\text{O}_4)_1$  is relatively radiation resistant. In more practical terms, this means that  $(\text{N}_2\text{O}_4)_1$  must receive a total dose in the tens of million rads, in order to produce 0.001 mole percent decomposition. To the missile scientist, this amply signifies that  $(\text{N}_2\text{O}_4)_1$ , as a powerful oxidant, would be stable by itself in fields of ionizing radiation, such as the van Allen belt and in solar flare drifts.

To the preparative radiation chemist, low G values mean that the velocity of the reverse reaction is greater than that of the forward reaction induced by radiation. Under such steady-state conditions reactive intermediates such as  $\text{N}_2\text{O}_5$ ,  $\text{NO}_2^+$ , and  $\text{NO}_2^*$  have prolonged half-lives in an ionizing field, thereby favoring the formation of reaction products with added constituents. When constituents such as benzene are added in small concentrations, relative to the  $(\text{N}_2\text{O}_4)_1$ , they would be expected to behave as scavengers and combine with most of the reactive intermediates. Opportunities for product formation could be considered multiple and promising with respect to types of products isolated. This would therefore serve as an indication of the variety of reactions possible under such conditions. Certainly,  $\text{N}_2\text{O}_5$  as a product of radiolysis, stabilized in a gamma field, should prove to be most conducive to the formation of products of interest in Ordnance chemistry.

## RECOMMENDATIONS

The results obtained in this initial study of the radiation chemistry of  $(\text{N}_2\text{O}_4)_1$  serve as a basis for optimizing conditions for product formation from the radiolysis of  $(\text{N}_2\text{O}_4)_1$  with added constituents. This work should therefore be continued in its second phase to include the isolation and identification of reaction products resulting from the scavenging of the multiple reactive intermediate species indicated herein.

In passing to this second phase of investigation, to more completely establish the proposed mechanism, the effect of NO on the radiolysis of  $(\text{N}_2\text{O}_4)_1$  should also be studied. The addition of NO to  $(\text{N}_2\text{O}_4)_1$  would be expected to have a decided effect on product formation since it appears that  $\text{N}_2\text{O}_3$  or its equivalent NO must play an important role in the mechanism of  $(\text{N}_2\text{O}_4)_1$  radiolysis (See Equations 9-13 in "Conclusions").

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Contract AT (30-3) - 321
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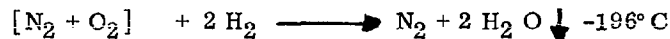
## APPENDIX

### Sample Calculations

#### Oxygen Analysis, Platinum Filament Combustion Method.

The formula,  $\frac{P_T - P_R}{3 P_I} \times 100 = \%O_2$ , used in this analysis is based on

the relationship given by the equation:



where  $P_I = \text{mm Hg } (N_2 + O_2)$

$P_T = \text{mm Hg } (N_2 + O_2 + H_2 \text{ in xs})$

$P_R = \text{mm Hg } (N_2 + \text{xs } H_2),$

and one-third of the volume of gas contraction,  $(P_I - P_R)$ , is equivalent to the oxygen content in the gas mixture. This quantity of oxygen, represented by  $(P_T - P_R) \times 0.333$  over the  $O_2/N_2$  mixture,  $P_I$ , gives the fraction of oxygen. For an actual determination, the pressure reading in the capillary of the McLeod gage is squared, viz., mm Hg x mm capillary length =  $(\text{mm})^2$  Hg-capillary length. Since the quantity,  $7.8 \times 10^{-4}$  cc per mm capillary length is a constant multiple factor, it was eliminated and the resultant values in units of  $(\text{mm})^2$  Hg in the fraction of pressure readings then cancelled out.

#### Specific Gas Volume Determinations [cc (Gas) STP/g $(N_2O_4)_1$ ]

These determinations were made by using the following formula:

$$\frac{1.262 \times P^I \times F \times V \times T^\circ}{g \text{ Wt } (N_2O_4)_1 \times T^I \times P^\circ} = \frac{\text{cc (Gas) STP}}{g (N_2O_4)_1} = V_s$$

where 1.262 = factor giving total volume of gas collected

$T^\circ = 273^\circ K$ ;  $T^I = \text{observed } ^\circ K$

$P^\circ = 760 \text{ mm}$

$P^I = \text{mm Hg } (N_2 + O_2) \text{ gas fractionated at } -196^\circ C$   
or mm Hg  $(N_2O)$  gas fractionated at  $-130^\circ C$

$F = O_2 \text{ or } N_2 \text{ fraction}$   
or 1.0 in the case of  $N_2O$

V = calibrated volumes, 2.39 or 5.40 cc

For very small V, when pressure readings are taken from the capillary section of the McLeod gage

$$P' = P^2 = [\text{mm Hg} \times \text{mm capillary length}] (N_2 + O_2) \text{ or } (N_2O), \text{ and}$$

$$V = V' = 7.8 \times 10^{-4} \text{cc/mm capillary length.}$$

#### G-Value Calculations

The following formula was used in calculating G values:

$$G = \frac{V \times v}{W \times T \times R \times r(f)} = \frac{\text{no. molecules}}{100 \text{ ev absorbed}}$$

where: V = number of cc at STP

$$v = 2.688 \times 10^{19} \text{ molecules / (cc) STP}$$

W = weight of sample in grams

T = time of irradiation (usually in hours)

R = dose rate in rads/hour

$$r = 6.24 \times 10^{13} \text{ ev absorbed / weight of sample in grams}$$

f = correction factor for electron density differences\*

\*For the irradiation of a given system, the total number of electron volts (ev) absorbed by way of Compton interaction is dependent on electron density per unit weight and source intensity. Source intensity is measured with a Fricke dosimeter, consisting of an aqueous solution of ferrous sulfate in 0.8N H<sub>2</sub>SO<sub>4</sub>. The calculated total dose absorbed must therefore be corrected for the difference between the electron density of the liquid N<sub>2</sub>O<sub>4</sub> and that of the dosimeter solution (per unit-weight). This correction factor, designated "f", is determined as follows:

Density of 0.8N H<sub>2</sub>SO<sub>4</sub> = 1.0229, or wt (1l soln) = 1022.9g

Equivalent weight of 0.8N H<sub>2</sub>SO<sub>4</sub> = 39.2g, or 0.4 moles H<sub>2</sub>SO<sub>4</sub>

Weight of water = 1022.9 - 39.2 = 983.7g, or 54.65 moles H<sub>2</sub>O



Number of electrons / molecule  $\text{H}_2\text{O}$  = 10

Number of electrons / molecule  $\text{H}_2\text{SO}_4$  = 50

Therefore, total number of electrons / 0.8N  $\text{H}_2\text{SO}_4$  =  $(54.65 \times 10) + (0.4 \times 50) = 566.5$ . Number of electrons / g 0.8N  $\text{H}_2\text{SO}_4$  =  $566.5 / 1022.9 = 0.554$

1 liter  $\text{N}_2\text{O}_4$  weighs 1447.0 g; number moles =  $1447/92 = 15.74/1$

Number of electrons per molecule  $\text{N}_2\text{O}_4$  = 46

Total number of electrons per liter =  $15.74 \times 46 = 724 \text{ e's/l}$

Number of electrons / g  $\text{N}_2\text{O}_4$  =  $\frac{724 \text{ e's/l}}{1447 \text{ g/l}} = 0.5$

Therefore  $f = 0.5/0.554$ .

An alternate method of calculating the G value is from the slope of the curve in terms of  $\text{cc(gas)STP/g (N}_2\text{O}_4)_1$  on the ordinate rise over the corresponding dose increment on the abscissa, i.e.,

$$\frac{Vs}{D} = \text{slope}$$

where  $Vs$  = specific gas volume =  $\text{cc(gas)STP/g sample wt} = \frac{V}{W}$

and  $D$  = total dose =  $T \times R$

then  $\frac{Vs}{D} \times \frac{v}{r(f)} = G$

Calculation of G ( $\text{N}_2\text{O}_5$ ) Formation from Irradiated ( $\text{N}_2\text{O}_4$ )<sub>1</sub> With and Without Oxygen Added.

The G ( $\text{N}_2\text{O}_5$ ) formation was calculated by the use of:

$$\frac{Vs}{D} \times \frac{v}{r} = G$$

where  $V_s$  is the specific volume of oxygen, and the rate of oxygen build-up given by  $V_s/D$  is equivalent to the rate of  $N_2O_5$  formation.

$(N_2O_4)_1$  plus  $O_2$

The rate of  $N_2O_5$  formation was obtained from the slope of the oxygen curve in Figure 10, viz.,

$$\frac{1.7 \times 10^{-2} \text{ cc } (O_2)/g}{20 \text{ Mrad}} = 8.5 \times 10^{-4} \frac{\text{cc } (O_2)}{g - \text{Mrad}}$$

Multiplying this value by the dose rate gives the rate of  $N_2O_5$  build-up in cc  $(O_2)/g\text{-hr}$ , i.e.,

$$8.5 \times 10^{-4} \text{ cc } (O_2)/g\text{-Mrad} \times 0.382 \text{ Mrad/hr} = 3.25 \times 10^{-4} \text{ cc } (O_2)/g\text{-hr}$$

This rate of  $N_2O_5$  formation must be corrected by adding to it the rate of formation represented by the rate of  $N_2O_5$  decomposition after irradiation, viz.,  $1.0 \times 10^{-5} \text{ sec}^{-1}$  or

$$1.0 \times 10^{-5} \text{ 1/sec} \times 3.6 \times 10^3 \text{ sec/hr} = 3.6 \times 10^{-2} \text{ hr}^{-1}$$

multiplied by the decomposition rate concentration, 0.125 cc  $(O_2)/g$  (taken from the mean of the curve in Figure 10), i.e.,

$$3.6 \times 10^{-2} \text{ hr}^{-1} \times 0.125 \text{ cc } (O_2)/g = 4.5 \times 10^{-3} \text{ cc } (O_2)/g\text{-hr}$$

The total  $N_2O_5$  buildup rate in terms of  $O_2$  is therefore:

$$0.325 \times 10^{-3} \text{ cc } (O_2)/g\text{-hr} + 4.50 \times 10^{-3} \text{ cc } (O_2)/g\text{-hr} =$$

$$4.825 \times 10^{-3} \text{ cc } (O_2)/g\text{-hr}$$

Dividing by the dose rate, the corrected rate of  $O_2$  uptake or  $N_2O_5$  formation is obtained in terms of cc  $(O_2)/g\text{-Mrad}$ , i.e.,

$$4.825 \times 10^{-3} \text{ cc/g-hr} \times \text{hr}/0.382 \text{ Mrad} = 1.26 \times 10^{-2} \text{ cc } (O_2)/g\text{-Mrad}$$

However, since the number of moles of  $N_2O_5$  equals twice the number of moles of  $O_2$ , the  $G(N_2O_5)$  formation is given by

$$G(N_2O_5) = \frac{2 \times 1.26 \times 10^{-2} \text{ cc } (O_2)/\text{Mrad} \times 6.02 \times 10^{23} \text{ molecules/mole}}{2.24 \times 10^4 \text{ cc } (O_2)/\text{mole} \times 6.24 \times 10^{17} \text{ ev/Mrad} \cdot 100 \text{ ev}} = 1.12$$

Pure  $(N_2O_4)_1$ :

The net rate of  $N_2O_5$  formation, in terms of  $\text{cc } (O_2)_n/\text{Mrad}$ , was obtained by subtracting the rate of oxygen accumulation at zero time after irradiation,  $\text{cc}(O_2)_z/\text{Mrad}$  (bottommost curve in Figure 6), from the total rate of oxygen accumulation as given by the upper-most curve,  $\text{cc}(O_2) \text{ th. eq.}/\text{Mrad}$ , as follows:

$$\begin{aligned} &0.30 \times 10^{-2} \text{ cc } (O_2) \text{ th. eq.}/\text{g-Mrad} - 0.065 \times 10^{-2} \text{ cc } (O_2)_z/\text{g-Mrad} = \\ &0.235 \times 10^{-2} \text{ cc}(O_2)_n/\text{g-Mrad} \\ \text{or } &0.235 \times 10^{-2} \text{ cc } (O_2)_n/\text{g-Mrad} \times 0.41 \text{ Mrad/hour} = \\ &0.096 \times 10^{-2} \text{ cc } (O_2)_n/\text{g-hr} \end{aligned}$$

Here again, the net rate of  $N_2O_5$  formation must be corrected by adding to it the rate of formation represented by the net rate of  $N_2O_5$  decomposition after irradiation. The net rate of  $N_2O_5$  decomposition was obtained by multiplying the rate constant of  $N_2O_5$  decomposition,  $1.0 \times 10^{-5} \text{ sec}^{-1}$  by the difference in the decomposition rate concentrations of  $O_2$  at 49 Mrads, given by

$$\left[ \frac{(O_2) \text{ th. eq.}}{g} - \frac{(O_2)_z}{g} \right], \text{ viz.,}$$

$$\begin{aligned} &1.0 \times 10^{-5} \frac{1}{\text{sec}} \times 3.6 \times 10^3 \frac{\text{sec}}{\text{hr}} \times \frac{(0.134 \text{ cc } (O_2) \text{ th. eq.} - 0.014 \text{ cc}(O_2)_z)}{g} = \\ &3.6 \times 10^{-2} \frac{1}{\text{sec}} \times 0.12 \text{ cc } \frac{(O_2)_n}{g} = 0.432 \times 10^{-2} \text{ cc } \frac{(O_2)_n}{\text{g-hr}} \end{aligned}$$

The total rate of  $N_2O_5$  formation is, therefore,

$$0.096 \times 10^{-2} \frac{\text{cc (O}_2\text{)}_n}{\text{g-hr}} + 0.432 \times 10^{-2} \frac{\text{cc (O}_2\text{)}_n}{\text{g-hr}} = 0.528 \frac{\text{cc (O}_2\text{)}_t}{\text{g-hr}}$$

Dividing by the dose rate, the total rate of  $\text{N}_2\text{O}_5$  formation is given in terms of cc  $(\text{O}_2)$  / g-Mrad, i.e.,

$$0.528 \text{ cc (O}_2\text{)}/\text{g-hr} \times \text{hr}/0.41 \text{ Mrad} = 1.29 \times 10^{-2} \text{ cc (O}_2\text{)}/\text{g-Mrad}$$

and finally,

$$G(\text{N}_2\text{O}_5) = \frac{2 \times 1.29 \times 10^{-2} \times 6.02 \times 10^{23}}{2.24 \times 10^4 \times 6.24 \times 10^{17}} = 1.11.$$

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<p>Accession No. _____ AD _____</p> <p>Picatinny Arsenal, Dover, N. J.</p> <p><b>COBAL T-60 GAMMA RADIOLYSIS OF LIQUID DINI- TROGEN TETROXIDE</b></p> <p>Thomas C. Castorina</p> <p>Technical Report 3072, May 1963, 62 pp, figures, graphs, tables. OMS 5011.11.838.001; Dept of the Army Project 599-25-001. Unclassified report</p> <p>The cobalt-60 gamma radiolysis of liquid dinitrogen tetroxide (<math>N_2O_4</math>) has been investigated as a function of variations in temperature, gas-to-liquid volume ratio, dose rates, and method of (<math>N_2O_4</math>) purification. The radi- olytic products are shown to be <math>N_2</math>, <math>N_2O</math>, and <math>N_2O_3</math>. The material balance of the <math>O_2</math> released at post-irradiation thermal equilibrium as compared with the calculated <math>O_2</math> derived from the production of <math>N_2</math> and <math>N_2O</math> from <math>N_2O_4</math> is</p> <p>(over)</p>	<p>1. Nitrogen oxides — Effects of radiation</p> <p>I. Castorina, Thomas C.</p> <p>II. Title</p> <p>UNITERMS</p> <p>Cobalt-60 Radiolysis Liquid Dinitrogen tetroxide Castorina, T. C.</p>
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